PB82-230798

A Comparative Evaluation of Seven Automated Ambient Nonmethane Organic Compound Analyzers

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Jun 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-230798

EPA-600/4-82-046
June 1982

A COMPARATIVE EVALUATION OF SEVEN AUTOMATED AMBIENT NONMETHANE ORGANIC COMPOUND ANALYZERS

January 1982

Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-82-046	ORD Report	PB82-230798

4. TITLE AND SUBTITLE	5. REPORT DATE
A COMPARATIVE EVALUATION OF SEVEN AUTOMATED AMBIENT NON-METHANE ORGANIC COMPOUND ANALYZERS	June 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Frederick W. Sexton, Raymond M. Michie, Jr. (RTI); Frank F. McElroy, Vinson L. Thompson (EPA)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Quality Assurance Department Research Triangle Institute Research Triangle Park, North Carolina 27709	11. CONTRACT/GRANT NO. 68-02-3222 and 68-02-3431
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	Final 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Automated hydrocarbon analyzers representing both conventional and state-of-the-art methods for ambient hydrocarbon monitoring were tested to evaluate their performance, comparability, and reliability under typical monitoring conditions. The resulting data and the statistical evaluation of those data are summarized and discussed. The test site and support equipment utilized during the study are also described, as are the quality control measures implemented to ensure the accuracy of the data collected.

The analyzers that were evaluated were the Beckman 6800 Air Quality Chromatograph, Bendix 8201 Reactive Hydrocarbon Analyzer, Mine Safety Appliance 11-2 Methane/Non-Methane Monitor, Meloy HC 500-2C FID Hydrocarbon Analyzer, Byron 404 NMVO Analyzer, HNU PI 201 Photoionization Monitor, and the Baseline 1030A Gas Chromatograph.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	111
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-600/4-82-046
June 1982

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This document was prepared
in cooperation with
the Research Triangle Institute
Research Triangle Park, NC 27709

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has responsibility for: assessing environmental monitoring technology and systems; implementing Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

As part of the assessment of environmental monitoring technology, this document summarizes an evaluation of seven non-methane organic compound (NMOC) analyzers. Although NMOC monitoring is not required, per se, such data are vitally important in some areas for planning the hydrocarbon control strategy necessary to achieve the National Ambient Air Quality Standard for ozone. This comparative evaluation of conventional and state-of-the-art NMOC analyzers should be beneficial to control agencies making ambient NMOC measurements with automated NMOC analyzers.

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ABSTRACT

Automated hydrocarbon analyzers representing both conventional and state-of-the-art methods for ambient hydrocarbon monitoring were tested to evaluate their performance, comparability, and reliability under typical monitoring conditions. The data resulting from this study and the statistical evaluation of those data are summarized and discussed. The test site and support equipment utilized during the study are also described, as are the quality control measures implemented to ensure the accuracy of the data collected.

The analyzers that were evaluated were the Beckman 6800 Air Quality Chromatograph, Bendix 8201 Reactive Hydrocarbon Analyzer, Mine Safety Appliance 11-2 Methane/Non-Methane Monitor, Meloy HC 500-2C FID Hydrocarbon Analyzer, Byron 404 NMVO Analyzer, HNU PI 201 Photoionization Monitor, and the Baseline 1030A Gas Chromatograph.

Simultaneous ambient non-methane hydrocarbon measurements (hourly averages) were collected from each analyzer over an 82-day test period. Each analyzer's readings are compared to each of the other analyzers' simultaneous readings and to separate analyses of samples by manual gas chromatography with flame ionization detection, using least squares linear regression and orthogonal regression techniques. Calibration and zero and span drift data are also presented. Statistical techniques are used to estimate the minimum detectable limit for each analyzer. Additional tests of the flame ionization detector in two of the test analyzers provided information on the response ratios to various specific hydrocarbon compounds and on the sensitivity of the response to minor changes in the operational fuel/air ratios.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

CRM	-- certified reference material
DAMDF	-- Durham Air Monitoring Demonstration Facility
DAS	-- data acquisition system
DVM	-- digital voltmeter
EKMA	-- empirical kinetic modeling approach
EMSL	-- Environmental Monitoring Systems Laboratory
EPA	-- U.S. Environmental Protection Agency
FID	-- flame ionization detector
GC	-- gas chromatograph(y)
kPa	-- kilo-Pascals
LOX	-- liquid oxygen
MSB	-- Methods Standardization Branch
NAAQS	-- National Ambient Air Quality Standard
NBS	-- National Bureau of Standards
NMHC	-- non-methane hydrocarbon
NMOC	-- non-methane organic compound
PID	-- photoionization detection
psig	-- pounds per square inch, gauge (i.e., above ambient pressure)
ppmC	-- parts per million as carbon
ppmV	-- parts per million as volume
RH	-- reactive hydrocarbon
RTI	-- Research Triangle Institute
SBFM	-- soap bubble flowmeter
SRM	-- standard reference material
TAD	-- technical assistance document
TNMHC	-- total non-methane hydrocarbon
TOC	-- total organic compound
URL	-- upper range limit, analyzer
url	-- upper range limit, recording device
UV	-- ultraviolet
WTM	-- wet test meter

SYMBOLS

CH_4	-- methane	H_2	-- hydrogen
C_2H_6	-- ethane	H_2O	-- water
C_2H_4	-- ethylene	NO_2	-- nitrogen dioxide
C_3H_8	-- propane	NO_x	-- oxides of nitrogen
C_4H_8	-- 2-methylpropene	O_3	-- ozone
C_6H_6	-- benzene	RCHO	-- aldehyde
CO	-- carbon monoxide	R_2CO	-- ketone
CO_2	-- carbon dioxide	SO_2	-- sulfur dioxide

ACKNOWLEDGMENTS

The authors gratefully acknowledge the invaluable assistance of Mr. William A. Lonneman and his staff of the Environmental Sciences Research Laboratory of the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, who provided the bag sampling and associated gas chromatographic analysis of the ambient and synthetic atmosphere samples.

We also acknowledge the statistical assistance from Mr. David Holland of the Data Management and Analysis Division of the Environmental Monitoring Systems Laboratory of the U.S. Environmental Protection Agency and Dr. Ty Hartwell and Ms. Corette Parker of the Statistical Methodology and Analysis Center of the Research Triangle Institute.

SECTION 1

INTRODUCTION

BACKGROUND

The National Ambient Air Quality Standard (NAAQS) for hydrocarbons, promulgated by the Environmental Protection Agency (EPA) in 1971 (1), is unique among the NAAQSs in that:

1. It was not based upon direct adverse effects on human health or welfare, but rather on the role that hydrocarbons play as precursors to the formation of ozone and other photochemical oxidants; and

2. It was intended solely to provide guidance for controlling hydrocarbon emissions to attain the NAAQS for ozone; compliance with the standard was not required per se.

Thus, the motivation for monitoring ambient hydrocarbons is not to determine compliance with the NAAQS for hydrocarbons, but to establish the degree of hydrocarbon emission control necessary to achieve the NAAQS for ozone and to monitor the effectiveness of that control. This distinction is important because it helps to clarify the type of hydrocarbon measurements needed.

Historically, ambient hydrocarbon concentrations were measured by direct injection of ambient air samples into flame ionization detector (FID). An FID responds to a wide range of hydrocarbon compounds; is quite insensitive to nonhydrocarbons; has a large, linear dynamic range; and is viable for continuous field operation (2). Although the per-carbon response of the direct-injection FID varies with the organic compound measured,* FIDs have nevertheless been widely used to measure ambient hydrocarbon concentrations (3). Also, continuous ambient hydrocarbon measurements have come to be more or less "defined" by the relatively characteristic direct-injection response of the FID (3).

In view of the role of hydrocarbons as precursors to ozone formation, it is clear that the reactivity, as well as the concentration, of the hydrocarbon is important. By far, the most prevalent ambient hydrocarbon is

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* It should be noted that modern FIDs used in chromatographic detectors and operating under highly controlled conditions with an inert carrier gas offer a much more uniform per-carbon response to various hydrocarbon compounds.

methane (CH_4), which occurs in urban environments and may reach three to five times the permanent geophysical concentration of 1.4 parts per million (ppm). CH_4 is formed by many natural processes and is quite nonreactive photochemically. Other hydrocarbon compounds vary in their photochemical reactivity, but none are as prevalent as methane in typical ambient air. Eliminating methane from hydrocarbon measurements provides a much more sensitive indicator of ozone precursor levels. Thus, most hydrocarbon measurements are described as non-methane hydrocarbons (NMHC) or total non-methane hydrocarbons (TNMHC). More recently, the description is given as non-methane organic compounds (NMOC) to include substituted hydrocarbons since the FID has some sensitivity to these compounds. Thus, NMOCs include the non-methane organic species from ethane up to the higher molecular weight organic compounds that appear in ambient air in the gas phase.

Development of continuous NMOC analyzers has been slow for a number of reasons, one being the lack of a suitable definition for measuring and expressing the concentration of this complex group of organic compounds. However, recent advancements in the development and verification of quantitative models (e.g., photochemical dispersion models) relating NMOC emissions and NMOC ambient concentrations to subsequent photochemical ozone concentrations now allow improved estimation of the degree of NMOC control necessary to achieve the NAAQS for ozone. NMOC data are a necessary input to these models, which are used to develop the ozone NAAQS attainment strategy. The requirements of the models serve to specify or define the nature of NMOC data needed.

Two general types of models are used: theoretical and empirical. Theoretical models predict ozone concentrations based on photochemical theory. They are generally very sophisticated and require a large data base including meteorological data, emissions data, and ambient concentration data for specific compounds or species. The hydrocarbon species data are usually obtained by manual gas chromatography with flame ionization detection (GC-FID). Additional continuous NMOC data obtained by automated FID analyzers are often obtained for verification or supplemental purposes. Empirical models are generally much simpler and are used to determine hydrocarbon control requirements from observed maximum ozone (O_3) concentrations and empirical oxides of nitrogen ($O_3/NMOC/NO_x$) relationships established from laboratory smog chamber research studies (4). One simple model, identified as the Empirical Kinetic Modeling Approach (EKMA), is widely used by control agencies for developing hydrocarbon control strategies (4).

NMOC MEASUREMENTS FOR USE IN EKMA

For NMOC measurements to be used in an EKMA model, they ideally should be made and expressed exactly as they were during development of the model. Exact duplication is not possible because of the differences between the smog chamber studies and the real atmosphere, but a reasonable approximation is possible.

During the smog chamber studies, a mixture of several low-carbon-number hydrocarbon compounds was formulated to simulate the ambient levels of auto

exhaust (the principal source of ambient NMOC) used in the chamber experiments. The automated FID analyzer used to monitor the hydrocarbon levels in the chamber was calibrated with each individual compound in the test mixture. The overall FID calibration was then determined by weighting its response to each compound according to the proportion of that compound in the total mixture. To the extent that the proportions of the compounds in the mixture represented the actual chamber contents, this technique effectively measured the true total concentration of the hydrocarbons present in the smog chamber.

For ambient air, a more accurate measurement process is manual gas chromatographic analysis, where the hydrocarbon mix is separated into individual components for measurement by FID. The use of an inert carrier gas provides a uniform response to a wide range of compounds and, if necessary, compound responses may be individually calibrated. For conventional automated FID analyzers monitoring ambient air by air injection, the per-carbon response of the FID varies with the organic compound being measured. Since individual compounds cannot be resolved, the overall response must be adjusted to approximate the average response of the ambient mix of organic compounds. As discussed later, FID response to an ambient mixture of organic compounds could be referenced to methane (commonly used in the past) but should be referenced to propane, as currently recommended, for uniformity.

Measurement of NMOCs are reported in parts per million carbon (ppmC). This unit is the concentration of the organic compound in parts per million by volume multiplied by the number of carbon atoms (carbon number) in the compound's molecular structure. For example, 10 ppmV C_3H_8 x 3 carbon atoms/molecule in C_3H_8 = 30 ppmC.

PROBLEMS ASSOCIATED WITH AUTOMATED FID ANALYZERS

Automated FID analyzers that measure ambient NMOCs have been available for a number of years and constitute the principal and almost exclusive method for measuring ambient NMOC continuously. Typically these analyzers determine the total organic compound (TOC) and CH_4 concentrations in ppmC separately, and the difference is used to determine the NMOC concentrations. CH_4 is separated from TOCs in one of two ways; either by separation in a gas chromatographic column or by selective oxidation of all other hydrocarbon compounds in a heated oxidizer.

Direct-injection, automated FID analyzers often suffer from a number of characteristic problems:

1. The detector's per-carbon response varies with the organic compound measured.

2. The detector's per-carbon response varies with the FID design and operating conditions.

3. Normal instrumental variability errors are substantially increased by the need to subtract two separate and independent measurements

to obtain NMOC and by the need for higher scale ranges to accommodate the TOC and CH_4 concentrations, which can be much higher than the NMOC difference.

4. The FID is susceptible to zero drift and possible interference from water vapor.

5. The lack of standardization of calibration procedures has resulted in calibrations based on CH_4, propane (C_3H_8), or other compounds depending on analyzer design or operator preference.

6. The FID requires hydrogen (H_2), which presents a degree of operational hazard.

In addition, analyzers using chromatographic separation of CH_4 from higher molecular weight organics are operationally complex and require higher levels of operator training and effort to maintain than most other types of ambient monitors.

PURPOSE

The primary objective of the study was to compare simultaneous measurements of several different automated conventional NMOC analyzers to determine the magnitude of discrepancies caused by the characteristic FID problems previously mentioned. A number of reports have documented these problems (3,5,6,7), but there appeared to be no extended ambient-air study to investigate their actual effect on typical NMOC monitoring data. A closely related objective was to quantify the typical minimum detectable sensitivity and variability of NMOC data among different analyzers.

A second major objective was to compare the ambient NMOC measurements from conventional NMOC analyzers to analysis by sophisticated, multicolumn, manual GC-FID. This sophisticated analysis is generally regarded as the most accurate and sensitive method for determining ambient levels of organic compounds. Although usually used to obtain concentrations of individual compounds or species, the various GC peaks can be summed to provide a measure of the total NMOC level. The manual GC-FID measurements also provide a common reference to which all of the NMOC analyzers can be compared.

A third objective of the study was to compare the two principal techniques for separating CH_4 from TOC in conventional NMOC analyzers. Both chromatographic and catalytic separation techniques are used in commercially available analyzers; it is important to determine if there are any significant differences between these two techniques.

Evaluation of the performance of nonconventional NMOC methods or measurement principles was the fourth objective. In recent years, several new techniques have become available that could offer significant advantages over conventional NMOC analyzers. An evaluation was necessary to determine their comparability to conventional NMOC methods.

The final objective was to gain operational experience and familiarity with the various commercially available NMOC monitors and to test and evaluate calibration techniques and quality assurance procedures. This information was needed for the preparation of a Technical Assistance Document (TAD) on NMOC monitoring (7). This TAD should assist NMOC monitoring agencies in obtaining good quality NMOC monitoring data.

The analyzers evaluated in the comparative analysis are listed in Table 1 together with each analyzer's principle of operation.

TABLE 1. LIST OF NMOC ANALYZERS EVALUATED

Analyzer	Principle of operation
Conventional	
Beckman 6800	Direct GC-FID
Bendix 8201	Direct GC-FID
Meloy HC 500-2C	Catalytic oxidation-FID
MSA 11-2	Catalytic oxidation-FID
Nonconventional	
Byron 404	Backflush GC-FID with oxidation/reduction to CH_4
Baseline 1030A	Backflush GC-FID with oxidation/reduction to CH_4
HNU PI 201	Photoionization by UV radiation

SECTION 2

CONCLUSIONS

The seven NMOC analyzers evaluated can be categorized as conventional or nonconventional. The four conventional analyzers (Beckman 6800, Bendix 8201, Meloy HC 500-2C, and MSA 11-2) employ techniques that have been used for years and are characterized by separate measurement of TOC and CH_4 by FID to obtain NMOC by difference. The three nonconventional analyzers measure NMOC directly. Two (Byron 404 and Baseline 1030A) use a backflush GC-FID technique with conversion of NMOC to methane. The other (HNU PI 201) uses a photoionization technique.

CONVENTIONAL ANALYZERS

The performances of the conventional and nonconventional analyzers were significantly different. With the exception of the Meloy analyzer, the conventional analyzers performed reasonably well during the second half of the 82-day ambient test period, after a variety of malfunctions and other problems that occurred during the first half of the test period were corrected. Calibration curves were linear with good correlation coefficients. Zero and span drifts were tolerable and in some cases quite low. In ambient air comparisons, the analyzers tracked well with each other, showing correlation coefficients of over 0.96 and agreeing with each other within 15 percent across the concentration range of the data, based on orthogonal regression analysis. The analyzers also agreed reasonably well with manual GC-FID analysis, with correlation coefficients over 0.96 and agreement (regression slopes) within 19 percent across the concentration range of the data. Statistically determined minimum detection limits ranged from 0.105 to 0.134 ppmC.

The Meloy analyzer showed erratic zero and span drift, poorer agreement with the other conventional analyzers and with GC analyses, and a considerably higher minimum detectable limit (0.320 ppmC). This analyzer was apparently not representative of conventional NMOC analyzers and, in any case, the manufacturer has indicated that it will be redesigned.

Additional tests of the FID used in two of the conventional analyzers indicated that the FID response pattern to various organic compounds was similar for FIDs of different design but operating with similar flow ratios. Tests also indicated that the response pattern was not particularly sensitive to minor changes in the operating flow ratios of the FID. Also, no significant difference was observed between the catalytic and chromatographic techniques for separating CH_4 from TOC.

The use of propane as the calibration standard for conventional analyzers is recommended, although data from this study are inconclusive as to selection of propane over methane. Preference for propane is based on the fact that FID response to propane appears to be more representative of the average response to NMOCs likely to be present in ambient air, while methane response is higher than the response of most other organic compounds. During the study, propane calibration provided good agreement between results from conventional analyzers (excluding Meloy) and manual GC-FID. Moreover, propane is one of the compounds that NMOC measurements are to include; methane is not. Lastly, direct-reading automated analyzers (which do not produce a CH_4 or TOC measurement) cannot be calibrated with methane but are generally calibrated with propane standards.

From the test results presented in Section 4, we conclude that conventional NMOC analyzers (other than the Meloy) are capable of providing NMOC measurements that agree reasonably well with each other and with manual GC-FID analysis provided that the analyzers are set up properly, are operating correctly, and are calibrated carefully and frequently. These provisions should not be underestimated, because each of the conventional analyzers tested seemed to be readily susceptible to either malfunctions or idiosyncratic problems of one sort or another. Nevertheless, once these characteristic problems are understood, the conscientious and meticulous analyzer operator can correct and overcome them and obtain good quality NMOC data. Reference 7 provides both general and analyzer-specific information on the conventional NMOC analyzers to assist operators in achieving this goal.*

NONCONVENTIONAL ANALYZERS

The performance of the nonconventional analyzers was inferior to that of the conventional analyzers. The Baseline backflush-GC produced a nonlinear response and excessive zero and span drifts, both of which were possibly due to integrator output problems. Additional problems with numerous flame-outs of the hydrogen FID flame prompted removal of this analyzer from the study. The Byron backflush-GC analyzer showed higher deviations from both the GC analyses and the conventional analyzers on ambient air, although it agreed well on cylinder standards and mixtures. Span drift was reasonable, but zero drift was somewhat erratic. In addition, regressing the ambient Byron readings on both the GC and the other analyzer's readings showed a substantial and unexplained zero offset.

The inferior performance of the two backflush-GC analyzers does not necessarily indicate that the backflush-GC technique is not viable. However, until more favorable performance data become available, we refrain from recommending use of this technique. Also, both Baseline and Byron offer direct GC type NMOC analyzers whose performance should not be judged by the observed performance of the backflush GCs.

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* The Meloy analyzer is not addressed in Reference 7 because the manufacturer has indicated that it is to be redesigned.

The photoionization technique used by the HNU analyzer is an ideal technique from an operational standpoint, but unfortunately its lack of response to CH_4, ethane (C_2H_6), propane, and other low-carbon-number compounds is apparently a substantial shortcoming. On ambient air, the analyzer read much lower than both the manual GC analyses and the conventional analyzers. Correlation was also rather poor. Again, in the absence of more favorable test data, use of the HNU analyzer for NMOC monitoring for purposes of the EKMA model is not recommended.

SECTION 3

TEST PROJECT DESCRIPTION

INTRODUCTION

During the summer of 1979, the Methods Standardization Branch, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency (EPA/EMSL-MSB), commissioned the Systems and Measurements Division of the Research Triangle Institute (RTI) to perform a comparative analysis of seven NMOC analyzers. These comparisons were performed under EPA contract 68-02-3222, Task 32, beween July 1, 1979, and October 1, 1979. The comparison was conducted under conditions similar to the MSB Phase II Postdesignation Test Procedures used for designated reference and equivalent methods. The test analyzers sampled from a common manifold and were operated as they would be under a typical air monitoring application to observe their long-term performance, reliability, and operational peculiarities. The comparison was performed at EPA's Durham Air Monitoring and Demonstration Facility (DAMDF) in Durham, North Carolina.

Several different techniques were used to evaluate and compare the seven analyzers. One technique was to pair the analyzers and compare simultaneous hourly ambient readings over an 82-day period. Another technique was to compare the analyzers' readings to manual GC-FID analysis of bag samples of the air taken at the same time. Similar comparisons were also carried out with atmospheres containing a blend of specific organic compounds. Lastly, characterization of the FIDs in two of the analyzers was performed to quantify the effects of variations in sample and hydrogen flow rates, variations in the burner air flow rate, and variations in the sample's oxygen content.

ANALYZER DESCRIPTIONS

The seven analyzers previously identified in Table 1 were compared and evaluated using the techniques previously mentioned. The Beckman, Bendix, Meloy, and MSA analyzers were considered to be conventional NMOC analyzers because each obtained NMOC concentrations by the conventional technique of measuring TOC and CH_4 concentrations separately, then subtracting the CH_4 concentration from the TOC concentration to obtain the NMOC value.

The Byron and Baseline analyzers were considered to be nonconventional NMOC analyzers because they obtained NMOC measurements directly without preliminary measurement of CH_4 or TOC concentrations. These conventional and nonconventional analyzers each utilized a hydrogen FID. The only non-FID type analyzer evaluated was the HNU, which relies on a photoionization

technique using ultraviolet light. This analyzer has known shortcomings (lack of response to low-molecular weight hydrocarbons) but uses a simple measurement principle, requires no hydrogen, and is very easy to operate. It was included in the study in the hope that it might prove conditionally acceptable.

The conventional analyzers utilize either of two techniques to separate the CH_4 component from the balance of the TOC. The MSA and Meloy models use catalytic oxidation to oxidize all organic compounds except CH_4. The Beckman and Bendix models use GC to separate methane from the other organic compounds. The GC separation method used by these conventional analyzers is considerably more complex than the catalytic oxidation due to the need for carrier gas, heated columns, and critical timing.

The nonconventional analyzers were similarly complex because these analyzers also used chromatographic techniques to separate CH_4 from NMOCs, which are retained on a column and later backflushed from the column for direct measurement by the FID. Both the Byron and the Baseline analyzers converted the backflushed organics to CO_2 and then to CH_4 before measurement by the FID. The purpose of this conversion was to avoid the characteristic response variation of the FID to different organic compounds. By converting all organic compounds (except CH_4) to CH_4, the instrument should be directly responsive to carbon number regardless of the identity of the original compound. Prior to the start of the study, this conversion-to-methane feature appeared very attractive. However, in practice the technique proved to be less attractive because special arrangements were necessary to avoid including the carbon dioxide (CO_2) peak from the original sample, which emerges from the column close to the two-carbon-compound (C_2) peaks, in the NMOC measurement. Such special arrangements are not necessary if the NMOCs are backflushed directly into the FID without conversion to CH_4. It is unfortunate that a direct backflush instrument was not included in the study.

Specific details and descriptions of each test analyzer follow.

Beckman Model 6800 Air Quality Chromatograph

This analyzer operates on the principle of chromatographic separation of CH_4 from TOC, with independent measurement of CH_4 and TOC by FID. During each 5-minute measurement cycle, a measured sample volume is injected directly into the FID to measure the TOC concentration. Following the TOC measurement, a second, separate sample is injected into a stripper column to separate CH_4 and carbon monoxide (CO) from CO_2 and high molecular weight organics. A GC column then separates CH_4 from CO prior to measurement by the FID. Subtraction of the CH_4 readings from the TOC readings results in the NMOC measurements. Ordinarily, this subtraction must be performed external to the analyzer. However, the analyzer tested had been modified to perform this subtraction electronically within the analyzer. As in any cyclic GC analyzer, the timing of flow control valves and signal gates is critical to proper operation. It is therefore imperative that the sequencer that controls the timing function be properly and accurately programmed.

Bendix Model 8201 Reactive Hydrocarbon Analyzer

This analyzer also operates on the principle of chromatographic separation of CH_4 from TOC, with independent measurement of CH_4 and TOC by an FID. The analyzer contains one FID and one sample loop. At the start of the 200-second cycle, sample is directed from the sample loop into the GC column. The CH_4 component of the sample emerges first and is injected into the FID for measurement. As the column is backflushed, another sample from the sample loop is routed directly to the FID for measurement of TOC. Internal subtraction of the CH_4 and TOC measurements results in the NMOC measurement. As in any cyclic GC analyzer, the timing of flow control valves and signal gates is critical to proper operation. It is therefore imperative that the sequencer that controls the timing functions be properly and accurately programmed.

Meloy Model HC 500-2C FID Hydrocarbon Analyzer

This analyzer operates on the principle of catalytic separation of CH_4, with separate measurement of CH_4 and TOC by FID. The analyzer employs a cyclic operation, dual-channel, single-detector design to allow measurement of the CH_4 and TOC in the air sample. During the 5-minute measurement cycle, sample is first injected directly into the FID for measurement of the TOC concentration. Following the TOC measurement, sample is passed through the catalytic oxidizer to oxidize all organics except CH_4. This component is then passed into the FID for measurement of the CH_4 concentration. Internal subtraction of the CH_4 measurement from the TOC measurement results in the NMOC measurement. The temperature of the oxidizer must be controlled accurately to ensure oxidation of all nonmethane compounds without oxidation of CH_4.

The design of the Meloy FID was unlike any of the other FIDs tested. The Meloy FID was similar to that of a flame photometric burner, which does not have a blanket of air surrounding the flame. Re-evaluation of this detector has been initiated by the manufacturer, and a new detector and analyzer design is expected.

Mine Safety Appliances 11-2 Methane/Non-methane Monitor

This analyzer operates on the principle of catalytic separation of CH_4, with separate measurement of CH_4 and TOC by FID. The analyzer employs a dual-channel design with two FIDs to allow continuous, simultaneous measurement of the CH_4 and TOC components in the sample.

The MSA 11-2 continuously splits the ambient sample into two portions for passage to the separate FIDs. One portion of the sample passes directly to FID #1, where TOC concentration is measured. The other portion passes through a heated cutter (Hopcalite® is used to oxidize all hydrocarbons other than CH_4 to CO_2 and H_2O) prior to entering FID #2, where the remaining CH_4 concentration is measured. The CH_4 measurement is then continuously subtracted from the TOC measurement to produce the NMOC measurement. The temperature of the oxidizer must be controlled accurately to ensure oxidation of all nonmethane compounds without oxidation of CH_4.

Byron 404 NMVO Analyzer

This analyzer operates on the principle of chromatographic separation of methane from the ambient sample, followed by backflush of the nonmethane organic compounds through a methane converter into an FID. During a measurement cycle, NMOCs are first separated from CO, CO_2, and CH_4 by a GC column. The retained NMOCs then are backflushed off the column into a catalytic oxidizer, which oxidizes all organics into CO_2. This CO_2 is then passed through a methanizer where it is reduced to CH_4 and injected into the FID for direct measurement of the ionized carbon atoms. As in any cyclic GC analyzer, the timing of flow control valves and signal gates is critical to proper operation. It is therefore imperative that the sequencer that controls the timing functions be properly and accurately programmed.

Baseline Series 1030-A Gas Chromatograph

This analyzer operates on the principle of chromatographic separation of CH_4 from the ambient sample, followed by backflush of the NMOCs though a methane converter and into an FID. During the first portion of the measurement cycle, the column is foreflushed with the sample to allow the CO, CO_2, and CH_4 to proceed through and out of the column. The last part of the measurement cycle consists of backflushing the column with carrier gas (air) to remove the retained NMOCs. These NMOCs are passed through a catalytic oxidizer to oxidize them to CO_2, and a methanizer, where the CO_2 is reduced to CH_4. This CH_4 is then measured by the FID to produce the measurement signal output. The model 1030-A contains a microprocessor that enables programmable control of measurement cycles and sample transport. The test monitor is configured to output only NMOC concentrations.

HNU Model PI 201

This analyzer is designed to measure ambient NMOCs in a sample by photoionization detection (PID). During the continuous measurement, the sample is directed to an ionization chamber where exposure to UV radiation occurs. The PID does not respond to CH_4, C_3H_8, nor other C2-C4 (and possibly higher) paraffins. The other NMOCs are ionized and measured by the detector, which produces a voltage output proportional to the other NMOC concentrations. No columns, valves, or hydrogen are required in this analyzer.

TEST SITE DESCRIPTION

The NMOC study was conducted at a site in an urban-industrial-commercial area of Durham, North Carolina. Ambient sample air for the analyzers was drawn from an intake on the building roof and distributed by an all-glass, power-ventilated manifold system. The system included a spiking manifold (for pollutant augmentation), a 1-liter mixing chamber, 12 sampling ports, and an outlet flowmeter used to determine the supplemental pollutant concentration. During pollutant augmentation, all sample air analyzed contained at least 90 percent unaltered ambient air. The building interior was temperature controlled to standard air monitoring instrument environmental temperatures.

ANALYZER SETUP

All instruments were operated on a 0 to 10 ppmC range. The analyzers' inlets were connected to a common manifold through Teflon® particulate filters (5 μm pore size) and either 3-mm (1/8-in) or 6-mm (1/4-in) o.d. FEP Teflon® tubing, depending on the analyzers' flow demand. The sample lines were kept as short as practical and none exceeded 3 m (10 ft).

All analyzers were set up during the first week of July 1979 and were fully operational by the end of the month. A five-point calibration was performed on all channels to assess linearity of instrumental response and to establish initial slope and intercept values for the calibration curves. All channels produced a linear response except the Baseline analyzer. This analyzer displayed a nonlinear response during calibration that, together with other problems, eventually resulted in its removal from the study. Multipoint calibrations were repeated at the middle and end of the study, with zero and span checks performed at least twice weekly.

DATA ACQUISITION

Two methods of data recording were utilized during the study: strip chart recorders and a data acquisition system. Each analyzer was continuously monitored by either a Leeds and Northrop (L/N) or an Esterline Angus (EA) strip chart recorder. The EA recorders were offset by 5 percent of chart to allow recording of negative responses. The L/N recorders could not be offset, and thus negative responses could be quantified only via the data acquisition system.

A Monitor Labs 9300 Data Acquisition System was connected to all analyzer hydrocarbon channels and was able to record responses from less than zero to greater than 100 percent of chart. The system was programmed to read instrument response each minute and to output the average of 60 readings each hour. This output was recorded on a paper tape. From the paper tape, the data were manually transferred into a Hewlett-Packard 9831A desktop computer for reduction.

The study lasted 82 days, from July 30 to October 19, 1979. The complete data set thus consisted of 1,968 potential hourly averages for each output channel of the seven analyzers evaluated. These raw hourly readings in percent scale units were stored on a magnetic disk for processing by the 9831A computer. Also stored were analyzer identification information and the slope and intercept from the initial calibration of each analyzer. Zero and span data were stored directly in the data set as coded slope and intercept values, replacing the hourly reading at the time of the zero and span operation.

Separate data sets were used to store the analyzers' responses to the synthetic hydrocarbon samples, manual GC-FID data from ambient and synthetic samples, and data from the FID characterization study.

MANUAL GAS CHROMATOGRAPHIC PROCEDURE

Measurement of samples by GC-FID was not performed at the test site, so Tedlar bag samples were collected from the sample manifold while the automated analyzers sampled calibration gases, synthetic hydrocarbon mixtures, or ambient air. In all cases, good laboratory procedures were used in order to minimize light, temperature, and storage time effects on the samples prior to analysis.

The GC system consisted of a three-column separation followed by flame ionization detection. The system was calibrated with a standard tank containing the organic compounds listed in Table 2. For each of the three columns, silica gel (SG), dibutyl maleate (DBM), and M-Bis [M-phenoxy] benzene and apiezon (MBMA), an adjustment factor was calculated to relate the manual GC-FID response to the propane standard used to calibrate the NMOC channels of the automated analyzers.

TABLE 2. CALIBRATION STANDARDS FOR THE MANUAL GC-FID SYSTEM

Compound	ppbC	Compound	ppbC
Toluene	31.8	Isobutane	52.8
Trichloroethylene	29.7	n-Butane	34.2
O-Xylene	39.4	c-Butene-2	17.0
Isopropylbenzene	82.7	2-Methylpentane	23.9
Ethane	91.4	3-Methylpentane	27.2
Ethylene	75.0	2,3-Dimethylpentane	20.4
Propane	93.8	2,2,4-Trimethylbutane	20.4
Propylene	75.4		

QUALITY CONTROL PROCEDURES

Flow Measurements and Control

Flow measurements for gas dilution were made with either an NBS-traceable soap bubble flowmeter (Hastings Model HBM-1, S/N 33) or a 3-L/rev wet test meter (American Model AL 18-3, S/N 15739) traceable to an EPA-maintained 600-L gasometer. All flow measurements were taken in triplicate, with time measured by a Heuer 413 Microsplit electronic stopwatch.

Flow rates were controlled by Tylan mass flow controllers. The Tylan controllers are reported to control flows to 3 percent, and theoretically maintain span concentrations independent of temperature and pressure variations during the span. However, to document standard flows during each zero/span, barometric pressure was measured with a mercury column barometer, and temperature in the flow measurement area was measured with a mercury thermometer. Flow rates were then measured and corrected to standard conditions of 760 mm Hg and 298 K.

Calibration Gases

Calibration materials were carefully chosen to eliminate as many potential inaccuracies as possible. The known FID characteristic response difference between CH_4 and C_3H_8 was investigated on detectors from two different analyzers. In both cases, response to CH_4 was found to be approximately 30 percent greater than response to C_3H_8. Since the response to C_3H_8 was found to approximate the average response to NMOCs commonly found in ambient air, C_3H_8 was selected for calibrating the NMOC channels. A CH_4 standard was necessary, of course, to calibrate the CH_4 and TOC channels because of the importance of balancing the channel's responses to ensure accurate subtraction of CH_4 from TOC. The HNU analyzer responded to neither CH_4 nor C_3H_8, so 2-methylpropene(isobutylene, C_4H_8) was used for calibration, as suggested by the manufacturer.

Zero air was generated from ambient air at the test site. Air from outside the building was compressed and passed through a permeation dryer, a silica gel column, an activated charcoal column, and two parallel-connected MSA catalytic oxidizers set to operate at 340 $\pm$ 10° C (644 $\pm$ 10° F). At this point the air was hydrocarbon-free and was available as zero air to all analyzers.

The CH_4, C_3H_8, and C_4H_8 gas standards were supplied by Scott Environmental Technology, Inc., in aluminum cylinders. The concentration of each standard was approximately 1,000 ppm, and each standard also included 321 to 335 ppm carbon dioxide and 20.6 to 20.8 percent oxygen in a pure nitrogen balance. These carbon dioxide and oxygen levels were chosen to simulate ambient air.

Calibration Gas Certifications

Two methods were used to verify the actual quality of the zero air. The first method was a comparison of the station zero air to a cylinder of 0.1-grade zero air supplied by AIRCO Specialty Gases that was independently analyzed as having less than 0.1 ppm hydrocarbons. In this analysis, all seven analyzers obtained stable zero traces on the station zero air prior to switching to the cylinder zero air. No substantial differences in responses could be detected between the two zero air sources.

The second method used to verify the quality of the station zero air was analysis by manual GC-FID. For this analysis, the Gas Kinetics and Photochemistry Branch of EPA's Environmental Science Research Laboratory obtained bag samples of the zero air and performed the analysis using the same three-column gas chromatograph system used to analyze bag samples of ambient air. The resulting chromatograms indicated that essentially no hydrocarbons were present in the station zero air.

The CH_4 working standard was referenced to a National Bureau of Standards SRM 1659a, supplied by the EPA Quality Assurance Branch. The referencing procedure was performed by obtaining responses to the primary standard on the CH_4 and TOC channels of the Beckman and Bendix instruments. After stabilization, the primary standard was replaced by the

working standard, which was diluted with station zero air so that the responses were identical to the primary standard responses. At this point, the flow rates of the working standard and diluent air were measured using an NBS-traceable soap bubble flowmeter and a calibrated wet test meter, respectively. The concentrations determined by calculation from each channel's response were averaged to obtain the concentration of the working cylinder.

The propane working standard was referenced to NBS-SRM 1665, also supplied by the QA Branch of EPA. The referencing procedure was the same as that described for methane, except that only the Beckman and Bendix TOC channels were used to obtain the responses for the primary and working standards.

An NBS standard for C_4H_8 (used for calibration of the HNU analyzer) was not available; therefore, a GC-FID laboratory instrument was calibrated with a 99.9-percent pure research-grade C_4H_8 standard using a dynamic double dilution technique. The working standard concentration was then measured immediately following calibration.

Table 3 identifies the working standards used during the project and lists the concentration of each reported by the supplier. The final column contains the results of verification against the primary standards.

TABLE 3. COMPONENT ANALYSIS OF WORKING STANDARDS

Cylinder number	Component	Specified concentration	Verified concentration
BAL - 914	CH_4	509 ppm	515.2 ppm
	CO_2	321 ppm	-
	O_2	20.7%	-
	N_2	Balance	-
BAL - 550	C_3H_8	1010 ppm	1037 ppm
	CO_2	335 ppm	-
	O_2	20.6%	-
	N_2	Balance	-
BAL -1055	C_4H_8	1000 ppm	1033 ppm
	CO_2	321 ppm	-
	O_2	20.8%	-
	N_2	Balance	-

Multipoint Calibration Procedure

By necessity, calibration procedures used for each of the various analyzers differed, depending on the measurement technique and the design configuration. Efforts were made, however, to keep the calibration proce-

dures, or at least the net result of the calibration, as uniform and comparable as possible for all the analyzers.

For the direct-reading Byron and Baseline analyzers, which had only an NMOC output channel, the calibration was straightforward; the analyzer's response was adjusted and related to various input propane concentrations via a calibration curve.

Calibration of the nondirect reading analyzers (Beckman, Bendix, Meloy, and MSA) was not so straightforward. Additional and preliminary calibration of CH_4 and TOC channels with methane was required. The specific procedure varied depending on the number of output channels, the number of span controls available, and whether the TOC-CH_4 subtraction was implemented on signals before or after they were processed by the span control circuits.

The Beckman analyzer normally has two output channels, CH_4 and TOC. As noted previously, the analyzer evaluated had been modified to provide a third NMOC channel, which was derived from electronically subtracting the CH_4 from the TOC signal. The CH_4 and TOC channels were calibrated and balanced to the methane standard. The NMOC channel was thus physically referenced to the methane calibration of the TOC channel. (This would also be the case when the NMOC readings are obtained by external subtraction of CH_4 from TOC.) NMOC response to propane was then obtained and related to propane concentrations by an empirical calibration relationship. This calibration relationship was subsequently applied to NMOC readings to achieve a propane-based calibration.

The Bendix analyzer had CH_4, TOC, and NMOC output channels. The CH_4 and TOC channel signals were adjusted with their respective zero and span controls prior to subtraction to produce the NMOC signal; therefore, the NMOC output was affected by the span settings of the CH_4 and TOC channels. The CH_4 and TOC channels were balanced with CH_4 to ensure accurate subtraction of the CH_4 from TOC. Following the balance operation, calibration of the NMOC channel with C_3H_8 was straightforward and similar to calibration of the direct-reading analyzers.

The Meloy analyzer had CH_4, TOC, and NMOC channels but only one span control. The CH_4 channel was calibrated with methane via the single span control. The TOC and CH_4 channels were then corrected slightly, if necessary, with trimmers for proper balance (TOC=CH_4 and NMOC=0) with methane, which resulted in the NMOC channel being physically calibrated to methane. The NMOC channel response to propane was then obtained and related to propane concentrations via a calibration curve relationship, which was used to interpret subsequent NMOC readings.

The MSA analyzer had only CH_4 and NMOC output channels. The CH_4 channel was first calibrated with methane. To balance the sensitivity of both FIDs, hydrogen flow to the CH_4 FID was shut off, as recommended by the manufacturer, to convert the NMOC channel to read TOC so that its response could be balanced to the earlier CH_4 channel's response. FID balance was achieved by adjusting H_2 flow. After balancing the FIDs on methane, the propane standard was sampled and the NMOC channel could be

spanned accordingly because the NMOC span control affected the NMOC signal after the TOC-CH_4 subtraction.*

Calibration of the direct-reading HNU analyzer with either CH_4 or C_3H_8 was not possible because the analyzer did not detect either compound. This analyzer was therefore calibrated with C_4H_8, as recommended by the manufacturer, and was the only analyzer not directly referenced to the C_3H_8 standard. However, the analyzer response was indirectly referenced to the C_3H_8 standard by adjusting the HNU data by a factor equal to the ratio of the average response of C_4H_8 to the average response of C_3H_8 on the conventional FID analyzers. This factor was determined to be 0.85. (See Figure 16.)

During all calibrations, hydrocarbon concentrations were measured or specified in parts per million carbon (ppmC). As noted previously, this unit of measure is defined as the product of the volumetric concentration (ppmV) and the number of carbon atoms per molecule of gas. For example,

10 ppmV C_3H_8 x 3 carbon atoms/molecule in C_3H_8 = 30 ppmC

10 ppmV CH_4 x 1 carbon atom/molecule in C_4H_8 = 10 ppmC.

Zero and Span Checks

After linearity was established in the initial multipoint calibration, the response curve for each analyzer was updated by periodic zero and span checks. Zero and span checks were made at least twice during each 7 days of operation, with adjustments made to the instrument if the zero response drifted in excess of 3 percent of full scale or if the span response drifted in excess of 7 percent from the calibration curve. Each zero and span response established a new slope and intercept that was used to correct subsequent ambient data up to the next zero and span check.

Routine Chromatograms

Instruments operating on the principle of chromatographic separation were routinely evaluated for proper operation through analysis of chromatograms. Chromatograms are "fingerprints" of the instruments' behavior and are useful in identifying potential operational malfunctions.

Data Validation

Raw data from the data acquisition system (DAS) were hand-entered into the Hewlett Packard 9831A computer. To validate the data base, all of the computer-printed data were proofed against the DAS output. To verify the DAS output, 10 percent of the data were manually reduced from the strip charts and compared to the DAS. Any discrepancies were investigated and corrected.

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*It was later determined that the channels could also (and more conveniently) be balanced by adjusting the NMOC channel to zero with CH_4 input without shutting off the hydrogen to the CH_4 FID.

SECTION 4

RESULTS AND DISCUSSION

This section provides a summary of the data collected during the evaluation of the seven automated hydrocarbon analyzers. Discussions are included, where necessary, to interpret the data and highlight the results.

OPERATOR'S COMMENTS

The following subsections provide subjective comments on the operation and maintainability of each analyzer evaluated. Also provided is a chronological history of each analyzer during the test period including malfunctions and unusual maintenance.

Comments on the Beckman 6800

1. The Beckman 6800 is no longer in production but may be available on the used-instrument market. Many of the original units sold in the early 1970s are still in operation or in serviceable condition. The model is patterned closely after the method description provided in Appendix E of 40 CFR Part 50 and provides an optional ambient CO measurement in addition to the hydrocarbon measurements. Normally the 6800 provides output signals only for TOC and CH_4 so that NMOC must be derived by external subtraction. However, the test unit used in the study was equipped with a special electronic circuit that carried out the subtraction internally and provided an NMOC output. Without these special electronics, it would have been the only unit in the study without a direct NMOC output.

2. The analyzer was large and heavy, thus requiring two men to move it. Three support gases were required for normal operation: hydrogen for the FID, dry air for valve actuation, and hydrocarbon-free zero air for carrier gas and burner air. A catalytic oxidizer was used to obtain a hydrocarbon-free supply of carrier gas. An external sample pump was also required. A modification allowed the pump to draw sample air through the analyzer's sample loops rather than to push it through as in the original configuration.

3. The analyzer contained one FID, measuring CH_4 and TOC alternately. The proper timing of the valves controlling sample transport was critical. The calibration procedure was complex and required a relatively high degree of dexterity and expertise; however, verification of the calibration curve through routine zero and spans showed the analyzer to be stable.

4. The analyzer required frequent attention to correct FID burner flame-outs, which were the only operational malfunctions. Valve failure was responsible for the flame-outs. Neither the original new valve, nor rebuilt valves prepared by the manufacturer or by EPA were reliable for more than 30 days of operation. Fast, stable responses to calibration gases were obtained during zero and span checks.

Chronological History of the Beckman 6800

Pre-1979: The analyzer was used in numerous field studies.

April 1979: New valves and columns were installed and trial monitoring began. Numerous FID burner flame-outs occurred.

June 1979: The analyzer was set up and started up at the monitoring station.

July 1979: The analyzer received a multipoint calibration. The response was linear.

7-23-79 to 7-31-79: Numerous FID burner flame-outs occurred. Efforts to resolve the problem were unsuccessful.

Days 213* to 214 (8-1-79 to 8-2-79): The manufacturer performed maintenance and troubleshooting on the analyzer.

Day 215 (8-3-79): Another multipoint calibration was carried out. Collection of valid ambient data began.

Day 223 (8-11-79): A flame-out occurred in the FID burner.

Day 235 (8-23-79): Multipoint calibration was performed following maintenance.

Days 237 to 249 (8-25-79 to 9-6-79): Numerous flame-outs occurred in the FID burner.

Day 250 (9-7-79): Valve A was replaced with a rebuilt valve.

Day 260 (9-17-79): Multipoint calibration was performed following maintenance.

Day 269 (9-26-79): A flame-out occurred in the FID burner.

Day 270 (9-27-79): Flame-outs continued to occur. Valve A was replaced with a rebuilt valve.

Day 292 (10-19-79): Data collection was completed.

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* Day numbers refer to the day of year, used as a convenient date identifier for computerized data files.

Comments on the Bendix 8201

1. This analyzer is a later generation GC containing only those components required for NMOC analysis (i.e., the unit has no capability to measure CO as described in Appendix E of 40 CFR Part 50). The analyzer tested was compact and light. Three support gases were required for normal operation: hydrogen for the FID, dry (ambient matrix) air for burner air, and hydrocarbon-free zero air for carrier gas. A catalytic oxidizer was used to obtain a hydrocarbon-free supply of carrier gas. Also, an external sample pump was required.

2. The analyzer contained one FID, with the CH_4 and TOC measured alternately. The timing of the valves controlling the various gas streams was critical. The calibration procedure was complex and required a relatively high degree of expertise; however, verification of the calibration curve through routine zero and spans showed the analyzer to be stable.

3. The test analyzer was initially set up and calibrated by the manufacturer in a manner that inadvertently lowered the analyzer's sensitivity to 2-methylpropene and (perhaps) higher carbon species. Troubleshooting identified the problem to be associated with the gate timing and with a buffer column (designed to suppress surges into the FID during valve actuation). The manufacturer replaced the column with a capillary and reset the timing. Detection of high carbon species was thereafter improved. An additional difficulty was traced to a burner thermistor that failed to detect a flame-out and thus engage the automatic ignition procedure. Increasing the thermistor sensitivity corrected this problem.

4. With the exception of the two difficulties previously mentioned, no other manufacturer involvement was necessary. Fast, stable responses to calibration gases were obtained during all zero and span checks. Little or no operator time was required to maintain the analyzer.

Chronological History of the Bendix 8201

Pre-1979: The analyzer was used in numerous field studies.

April 1979: Preliminary testing was conducted to verify operation.

June 1979: The analyzer was transferred to the monitoring station and was set up by the manufacturer (setup included rebuilding the valves).

Day 211 (7-30-79): The analyzer received a multipoint calibration. The analyzer's response to C_4H_8 was significantly depressed, being approximately 86 percent less than the calculated concentration. The collection of ambient data was initiated.

Day 247 (9-4-79): A flame-out occurred in the FID burner. The autoignition failed to relight the burner.

Day 248 (9-5-79): A Bendix serviceman reset the analyzer timing, replaced a buffer column, and adjusted the burner thermistor.

Day 260 (9-17-79): The analyzer was recalibrated.

Day 292 (10-19-79): Data collection was completed.

November 1979: Supplemental tests were conducted to characterize the FID response to various organic compounds.

Comments on the Meloy HC 500-2C

1. The analyzer tested was compact and light. Only one support gas (hydrogen for the FID) was required for normal operation. The test analyzer was set up to measure concentrations of methane, total organics, and non-methane organics.

Initial calibrations were hampered by a noisy response to station zero air. Noisy zero and span responses further complicated calibration attempts; thus, original analyzer serial number 8H126 was replaced by a similar model, serial number 7F075. Noise and drift problems were also present in this second analyzer, and it was replaced by the original analyzer (S/N 8H126), which had been modified. Modifications included installation of a hydrogen line filter, elimination of automatic zero and span operations, bypass of the air flow rotameter, and insertion of a needle valve in the TOC sample flow line to balance the THC and CH_4 response to a methane standard.

2. The analyzer contained one FID and measured CH_4 and TOC alternately. The timing of the valve controlling sample transport was much less critical than in chromatographic systems. The actual calibration procedure was not complex; however, confusion developed because of variations between the instrument manual's procedure and the manufacturer's verbal directions. (Options were available on the monitor that were not described in the manual.)

3. The unusually low response to propane (see Figure 3) may be related to the nonconventional FID burner. The analyzer was relatively simple to maintain and operate. The relative ease of operation was reduced, however, due to poor performance during initial calibrations. After obtaining a stable calibration, further difficulties were minimal.

Chronological History of the Meloy HC 500-2C

Pre-1979: The analyzer was used as a demonstrator model.

July 1979: The analyzer (S/N 8H126) was set up at the monitoring station by the manufacturer. Accurate calibration was not possible due to a noisy response to zero air and unstable response to span gas.

Day 207 (7-26-79): The analyzer was removed by the manufacturer for repair and maintenance.

Day 214 (8-2-79): A replacement analyzer (S/N 7F075) was installed by the manufacturer.

Days 215 to 233 (8-3-79 to 8-21-79): Unstable responses to calibration standards prevented accurate calibration.

Day 234 (8-22-79): The second analyzer (7F075) was replaced with the original unit (8H126), which had been modified.

Day 235 (8-23-79): The analyzer received a multipoint calibration. All channels responded linearly, but response to propane was very low. Collection of ambient data was initiated.

Days 249 to 291 (9-6-79 to 10-18-79): Unstable responses to calibration standards necessitated frequent analyzer adjustments.

Day 292 (10-19-79): Collection of ambient data was completed.

Comments on the MSA 11-2

1. The analyzer tested was large and heavy, thus requiring two men to move it. Only one support gas (hydrogen for the FID) was required for normal operation. The test monitor measured concentrations of methane and total organics, but provided signal outputs only for methane and nonmethane organics.

2. The analyzer used two FIDs. It was therefore important to balance the two channels with a methane standard so that the outputs from both detectors were equal when sampling methane. The manufacturer-recommended procedure required that the methane burner be extinguished by removing hydrogen flow. Reigniting the burner and obtaining identical sensitivity was a delicate operation that could cause error in the calibration. Subsequent to the study, a new calibration procedure that does not require extinguishing the methane burner was developed.

3. The continuous, dual-channel operation of the analyzer required no valves or gate timing procedures. The absence of these procedures greatly simplified the calibration of this analyzer and therefore allowed for operation by a less highly trained individual.

4. The analyzer had a fast response and a stable output. These assets were offset somewhat by the frequent flame-outs caused by moisture condensation in the cutter, distribution block, and FID. Maintenance performed to resolve the moisture problem was not difficult due to the simplicity of the system. Subsequent to the study, the moisture problem was substantially reduced by modification of the inlet sample conditioning system.

Chronological History of the MSA 11-2

Pre-1979: The analyzer, manufactured in 1976, was used in various laboratory studies.

January 1979: The analyzer was overhauled by the manufacturer.

January to June 1979: During preliminary monitoring, frequent flame-outs in the FID burners occurred.

Day 182 (7-1-79): The analyzer was set up in the monitoring station.

Day 184 (7-3-79): The manufacturer performed initial setup and calibrations. The oxidizer was replaced.

Days 184 to 192 (7-3-79 to 7-11-79): The thermistor in the cutter failed.

Day 200 (7-19-79): The thermistor was replaced by the manufacturer.

Day 212 (7-31-79): The analyzer received a multipoint calibration, and collection of valid ambient data began.

Days 243 to 264 (8-31-79 to 9-21-79): Moisture condensation in the cutter, distribution block, and FID burners caused numerous flame-outs.

Day 277 (10-4-79): The moisture trap was modified by adding a back-pressure regulator.

Day 292 (10-19-79): Collection of ambient data was completed.

11-79: An FID characterization study was performed to observe response to various specific organic compounds.

Comments on the Byron 404

1. The analyzer tested was compact and light. Three support gases were required for normal operation: hydrogen for the FID, service air for valve activation, and HC/CO_2-free air for carrier gas. Due to an apparent zero offset (zero response exceeded 1.0 ppmC), several methods of carrier gas generation were evaluated. Initial efforts were directed at scrubbing CO_2 from the station hydrocarbon-free zero air, but the upscale response to zero air remained. Therefore, HC/CO_2-free cylinder gas was supplied as carrier gas. The upscale response to zero air was still present, which prompted a change in the column temperature. Reducing the temperature lowered the background response significantly.

2. The analyzer contained one FID, which measured NMOC directly. The timing of signal gates and the valves controlling the various gas flows was critical. The timing was controlled by solid state components that were set by the manufacturer, thereby eliminating potential operator error. The calibration procedure was not complex.

3. The analyzer required frequent manufacturer involvement during the setup phase due to a zero offset problem. Although the problem was not eliminated, it was reduced significantly. Essentially no further manufacturer involvement was required during the study. The monitor's span response was very stable, thus reducing calibration complications. Minor zero drift corrections were necessary, however.

Chronological History of the Byron 404

Pre-1979: The analyzer was manufactured in 1979.

July 1979: The manufacturer installed the analyzer at the monitoring station. Changes in the carrier air and temperature of the chromatographic column were made to try to correct elevated responses to zero air. Response to zero air was improved but it was never lower than about 0.5 ppmC (with respect to the auto-zero generated internally).

Day 212 (7-31-79): The analyzer received a multipoint calibration, and collection of valid ambient data was initiated.

Day 285 (10-12-79): The sample pump's bearings were approaching failure so the manufacturer replaced the pump.

Day 292 (10-19-79): Data collection was completed.

Comments on the Baseline 1030-A

1. The analyzer tested was compact and light. Three support gases were required for normal operation: hydrogen for the FID, air for valve actuation, and nitrogen for carrier gas. Zero air was originally used as the carrier but was replaced with nitrogen after problems developed from moisture condensing in the methanizer.

2. During setup, it was discovered that the analyzer did not have the store-and-hold-type of continuous output signal required to interface with the data acquisition system. Consequently, the manufacturer attempted to design a suitable, makeshift interface circuit to allow the analyzer to be included in the study. The manufacturer claims that the improper operation of this makeshift interface, together with some moisture flooding, were responsible for many or most of the problems encountered with this analyzer, including lack of linear response during calibration, zero and span drift, loss of sensitivity, and frequent flame-outs. Baseline has subsequently indicated that the output signal interface has been redesigned and the moisture flooding has been corrected. The company has also indicated that it believes that the backflush GC technique is feasible but requires additional research and development before it will become practical.

Chronological History of the Baseline 1030-A

Day 191 (7-10-79): The manufacturer installed the analyzer at the monitoring station. The analyzer was new and had no previous history of operation. During installation, a pressure regulator was found to be inoperable and was replaced.

Day 192 (7-11-79): The methanizer malfunctioned because of an accumulation of moisture. The carrier air (supplied by scrubbing ambient air of hydrocarbons and carbon dioxide) was replaced with a cylinder of compressed nitrogen. The methanizer was replaced, and the analyzer was calibrated.

Days 204/205 (7-23/24-79): The FID flame went out on both days. Hydrogen pressure to the burner was increased to 165 kPa (24 psi).

Day 208 (7-27-79): There were erratic responses to calibration gases.

Day 211 (7-30-79): After the multipoint calibration, analyzer response was determined to be nonlinear.

Days 212 to 260 (7-31-79 to 9-17-79): Problems in the integration board resulted in a loss of data during each hourly average. Zero drift, slow response, and flame-outs hampered normal operation.

Day 261 (9-18-79): The analyzer was withdrawn from the study.

Comments on the HNU PI 201

1. The analyzer was compact and light. No support gases were required for normal operation.

2. The analyzer did not respond to methane or propane calibration gas. The manufacturer suggested the use of isobutylene (2-methylpropene, C_4H_8) as the calibration gas. The calibration procedure was simple and response to isobutylene was rapid and linear. Problems developed near the end of the study in obtaining a stable response to the span gas. Also, sensitivity dropped sufficiently to require adjusting the span pot to its maximum setting to maintain calibration.

3. Very little attention was necessary to maintain the monitor. Replacement of the high voltage board was suggested by the manufacturer to correct span drift. The absence of support gases greatly increased the ease of normal operations.

Chronological History of the HNU PI 201

Pre-1979: The analyzer was used as a demonstrator model prior to this study.

May 1979: The analyzer was overhauled by the manufacturer.

Day 191 (7-10-79): The analyzer was installed at the monitoring station by the manufacturer. Although the front-panel meter had been damaged in shipping, the multipoint calibration indicated that the response was linear.

Day 208 (7-27-79): Analyzer response to the span gas was unstable.

Day 211 (7-30-80): The analyzer received a multipoint calibration. Collection of ambient data was initiated.

Days 221 to 228 (8-9-79 to 8-16-79): Analyzer response to the span gas was unstable.

Day 239 (8-27-79): The high voltage board was replaced; however, unstable span responses continued to occur.

Day 243 (8-31-79): The span pot was at its upper limit. The manufacturer suggested continuing operation.

Day 292 (10-19-79): Collection of ambient data was completed.

CALIBRATION CURVES

Typical multipoint calibration curves for each analyzer are shown in Figures 1 through 7. In each curve, only the NMOC channel's response to the propane calibration standard is reported (with the exception of the HNU, which is calibrated with 2-methylpropene).

The figures illustrate the linear response of all the analyzers except the Baseline (see comments on the Baseline analyzer in the previous subsection on Operator's Comments). Also noted in the previous subsection was the Meloy's unusually low response to the propane calibration standard. A nonconventional FID burner design may have been the cause of this reduced response.

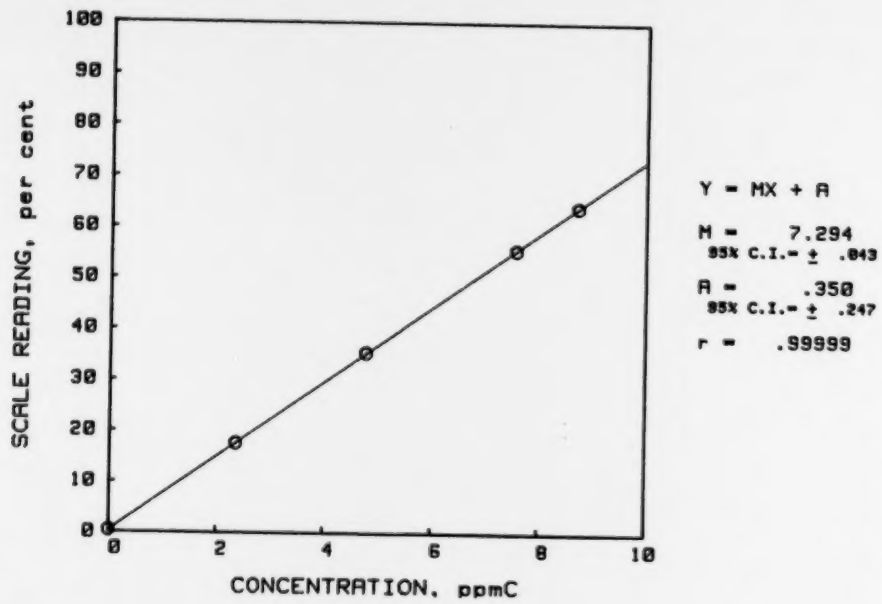


Figure 1. Typical propane calibration curve for the Beckman 6800 NMOC response. Date: 8/23/79 (day #235).

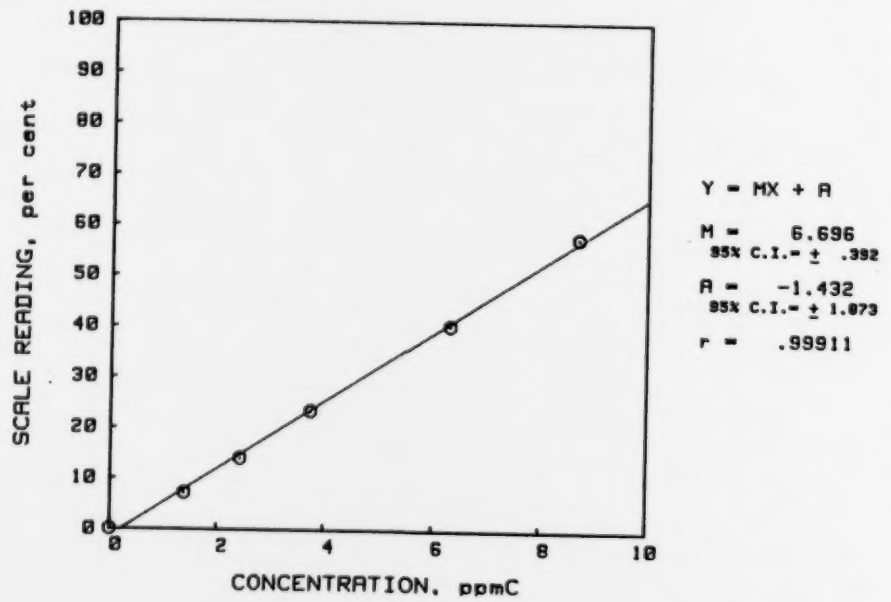


Figure 2. Typical propane calibration curve for the Bendix 8201 NMOC response. Date: 7/31/79 (day #212).

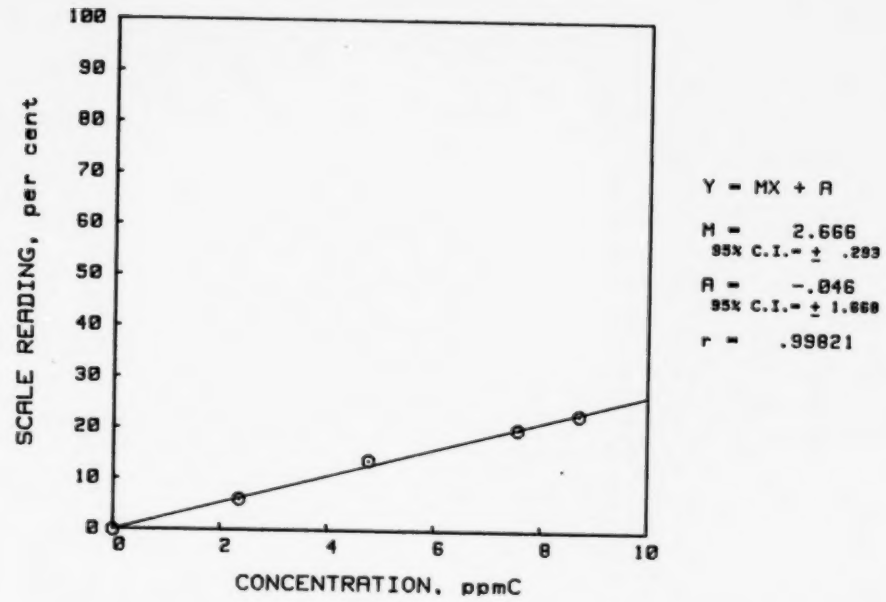


Figure 3. Typical propane calibration curve for the Meloy HC 500-2C NMOC response. Date: 8/23/79 (day #235).

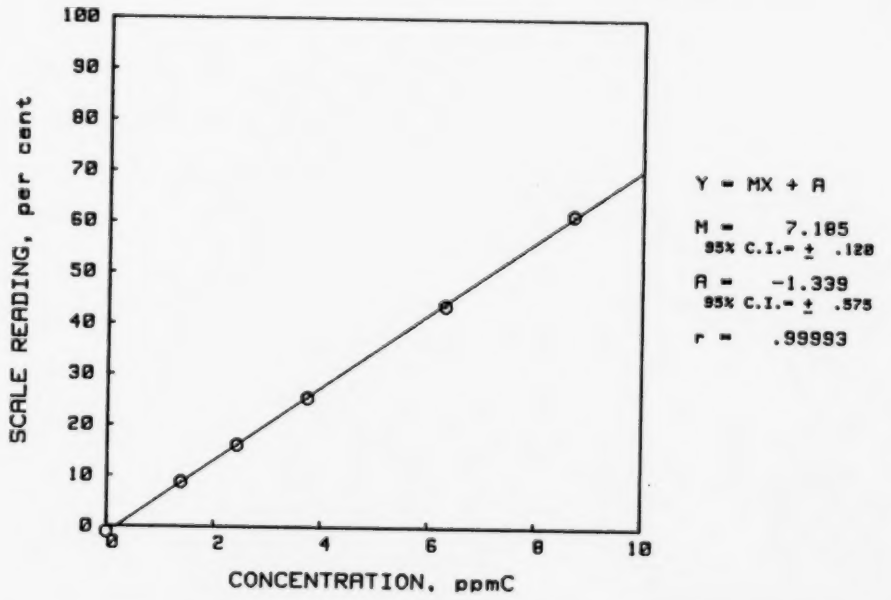


Figure 4. Typical propane calibration curve for the MSA 11-2 NMOC response. Date: 7/31/79 (day #212).

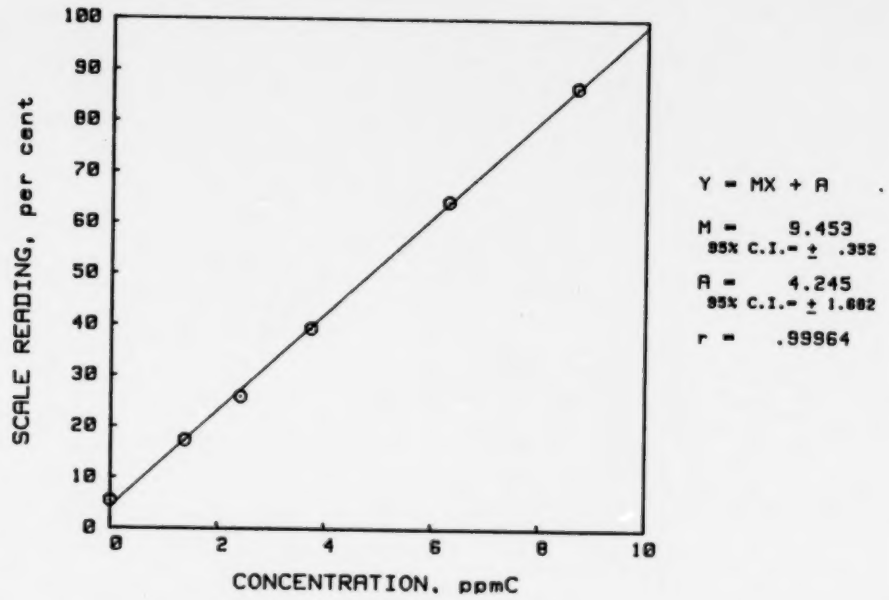


Figure 5. Typical propane calibration curve for the Byron 404 NMOC response. Date: 7/31/79 (day #212).

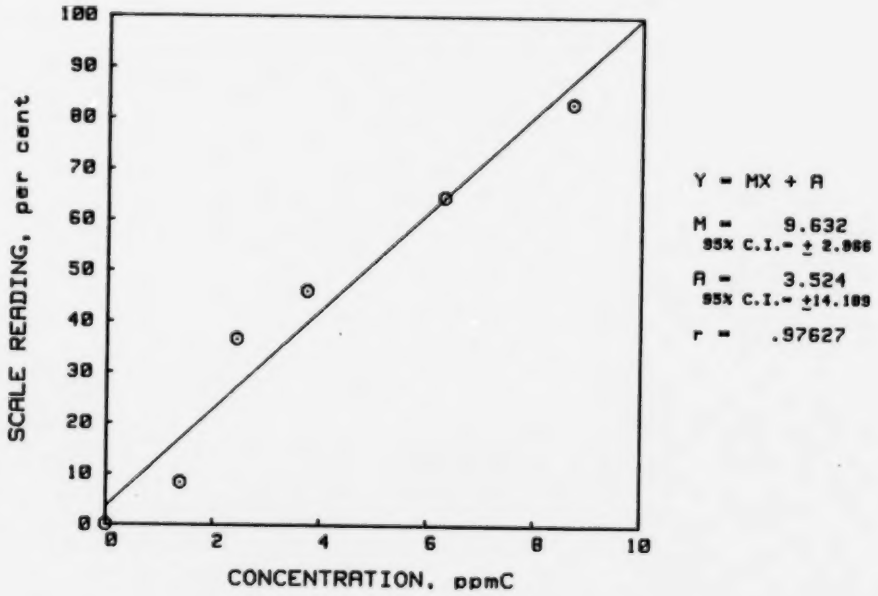


Figure 6. Typical propane calibration curve for the Baseline 1030-A NMOC response. Date: 7/31/79 (day #212).

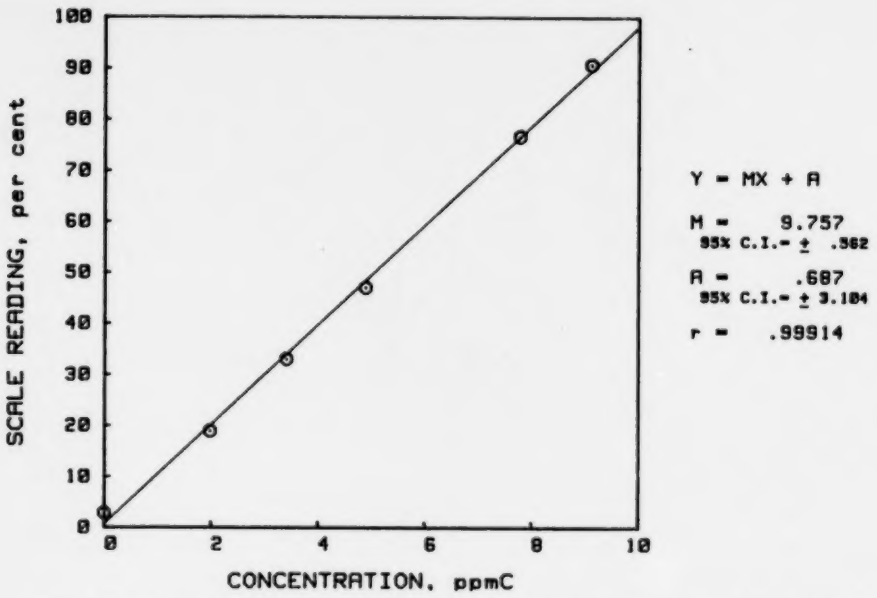


Figure 7. Typical isobutylene calibration curve for the HNU PI 201 NMOC response. Date: 7/30/79 (day #211).

ZERO AND SPAN STABILITY

A documented problem with automatic NMOC analyzers has been their zero drift and, to a lesser extent, span drift (3,5,6). This problem was investigated during the NMOC analyzer evaluation. Results of this investigation follow.

Zero and Span Corrections

As noted earlier, all analyzers sampled ambient air simultaneously from a common manifold during the 82-day test period. All analyzer responses were integrated into common 1-hour periods and recorded as hourly averages in percent-of-scale units. During computer analysis, each hourly reading was converted to concentration units according to the following equation:

$$X = (Y - A)/M \qquad (1)$$

where X = analyzer's response converted to ppmC;
Y = analyzer's raw (uncorrected) response in percent of scale;
A = intercept of the analyzer's calibration curve, percent of scale;
M = slope of the analyzer's calibration curve, percent of scale/ppmC.

The slope and intercept of the original multipoint calibration curve were updated after each zero and span check, thus the analyzer's raw readings were always corrected to the most recent calibration parameters.

The individual analyzer responses to span gas standards over the first 30 days of the study are illustrated in Figure 8, which also contains a sequential plot of the conventional analyzer's responses to ambient air. Responses to zero and span gas standards are considerably exaggerated in width to show both the unadjusted response (based on the slope and intercept from the previous zero and span check) and the adjusted response (based on the new slope and intercept). This illustration is not intended to show analyzer-to-analyzer comparisons, but to illustrate the range of the calibration concentrations, the frequency of zero and span checks, and the perspective between the NMOC concentrations of the standards and those in typical ambient air. (For the objectives of this study, there was no reason to restrict the usable ambient data to the 6 a.m. to 9 a.m. daily readings, as might be done during accumulation of data for use with the EKMA models.)

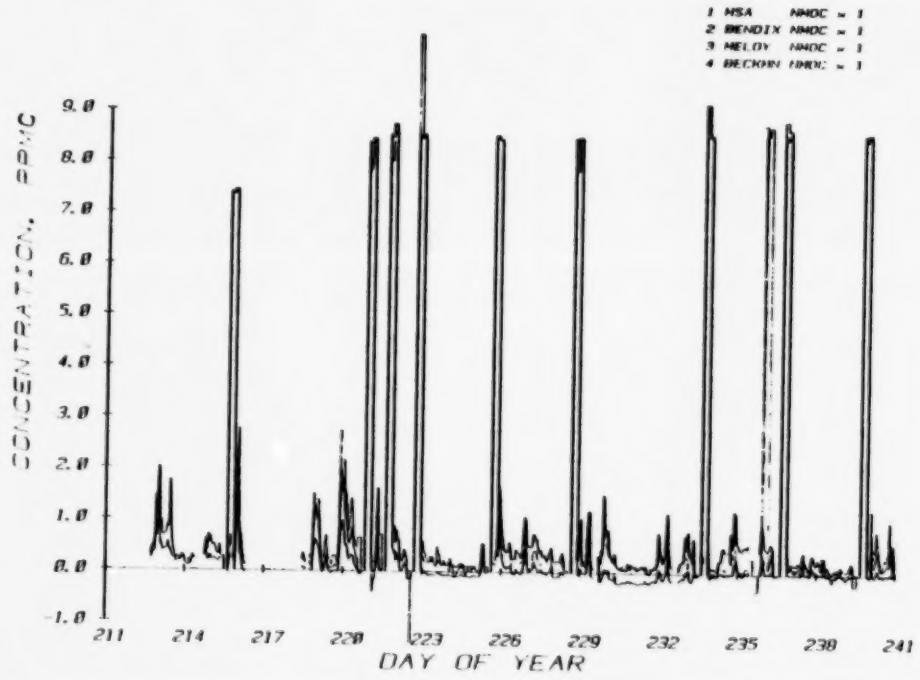


Figure 8. Sequential plot of four conventional analyzers' NMOC measurements of calibration standards and ambient air. The first step of each span or zero response is the unadjusted response; the second is the adjusted response.

Zero and Span Drift

In evaluating and comparing the various NMOC analyzers, an important characteristic is the zero and span stability of the analyzers. The cumulative zero and span drifts of the NMOC channels of the analyzers are plotted in Figures 9 through 15. The values in these plots are the accumulated drifts based on the initial analyzer NMOC calibration obtained at the start of the study. The initial slope and intercept for each analyzer are represented by the dashed horizontal line on its respective drift chart. Actual physical adjustments to the analyzer zero or span control are evidenced as nearly vertical segments of the traces. Since the hourly readings are all corrected based on the most recent zero and span reading, only the drift occurring from one zero or span check to the next affects the corrected data, not the total offset from the zero baseline.

The lack of stability of many of the analyzers, however, illustrates the importance of frequent zero and span checks, which should be used to correct the subsequent NMOC readings either by a physical adjustment to the analyzer or by computational corrections.

In comparing the conventional analyzers' drift between zero and span checks, the Beckman 6800 proved to be the most stable, with typical zero drifts less than 0.1 ppmC and typical span drifts less than 5 percent. The MSA and Bendix analyzers were less stable, showing zero drifts up to 0.2 ppmC and span drifts up to 8-10 percent. In addition to extended start-up problems, the Meloy analyzer exhibited serious difficulties with zero drifts, which ranged up to 0.6 ppmC, though span drift was less severe (approximately 10 percent). The nonconventional HNU analyzer showed problems with zero drift between 0.1 and 0.6 ppmC and span drift between 6 and 10 percent as well as a significant loss of sensitivity toward the end of the test period. The Byron was moderately stable except for several large zero drifts between 0.4 and 0.6 ppm near the middle of the study period. The Baseline instrument showed very erratic zero drift, which, together with previously mentioned problems, caused its withdrawal from the study.

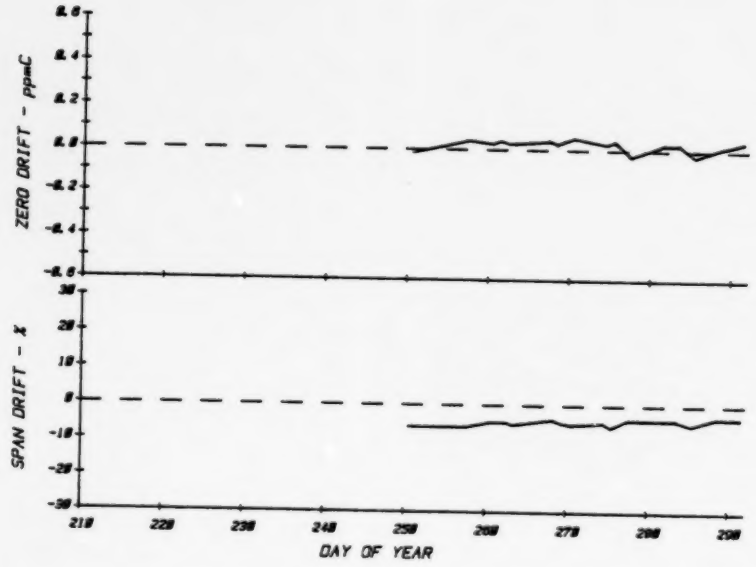


Figure 9. Beckman 6800 cumulative zero and span drift.

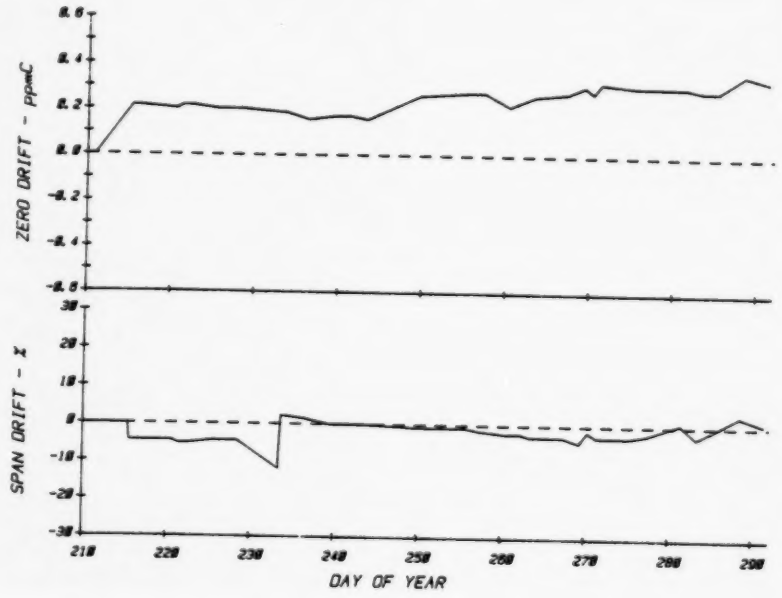


Figure 10. Bendix 8201 cumulative zero and span drift.

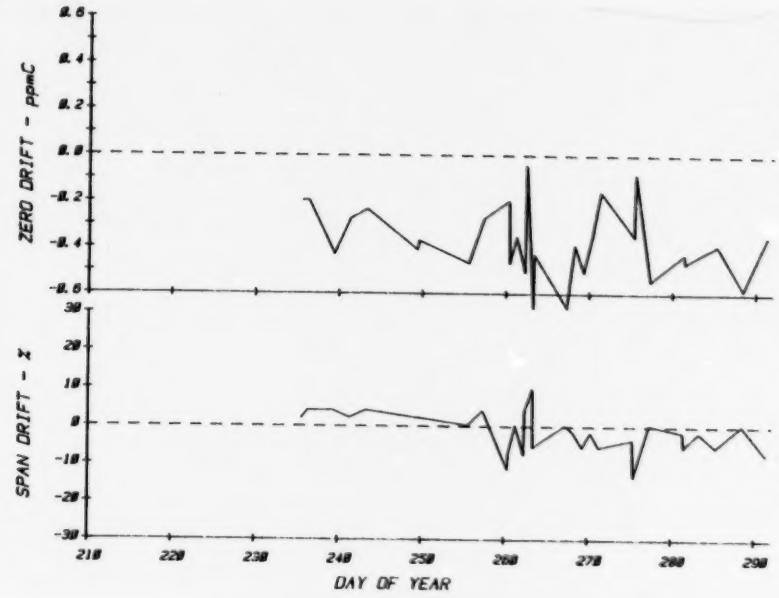


Figure 11. Meloy 500-2C cumulative zero and span drift.

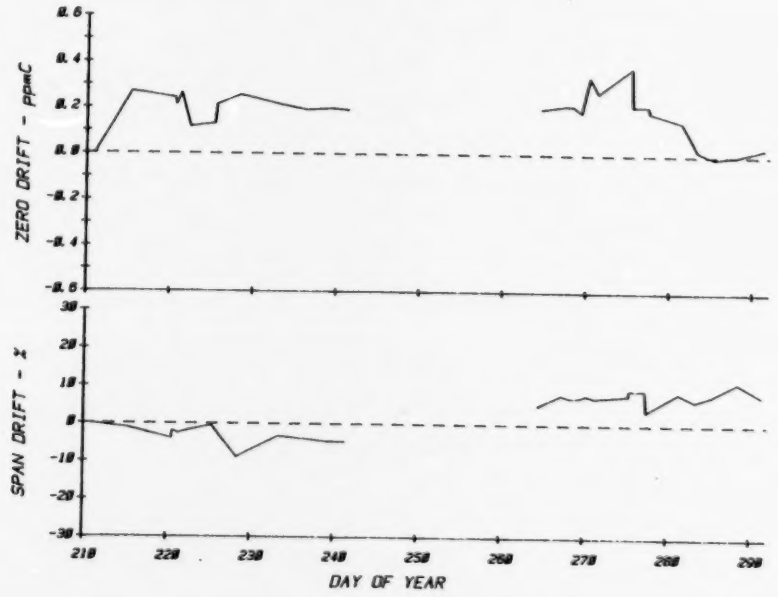


Figure 12. MSA 11-2 cumulative zero and span drift.

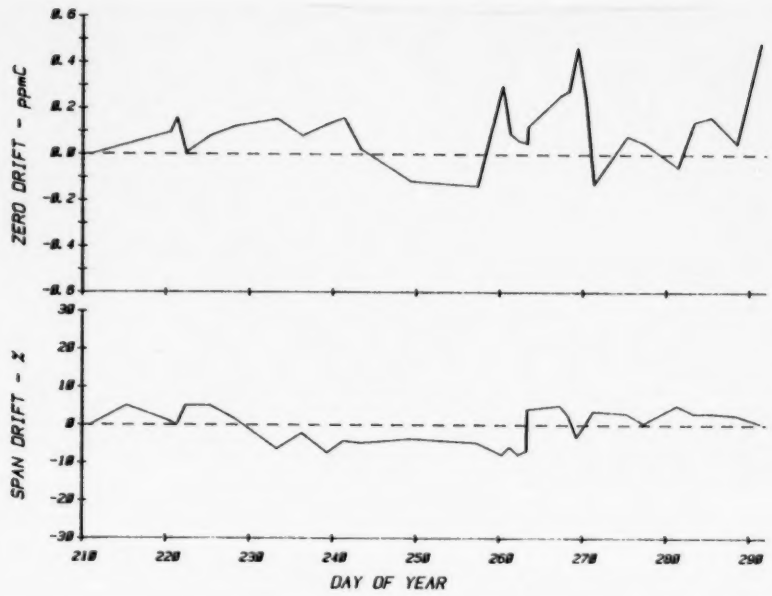


Figure 13. Byron 404 cumulative zero and span drift.

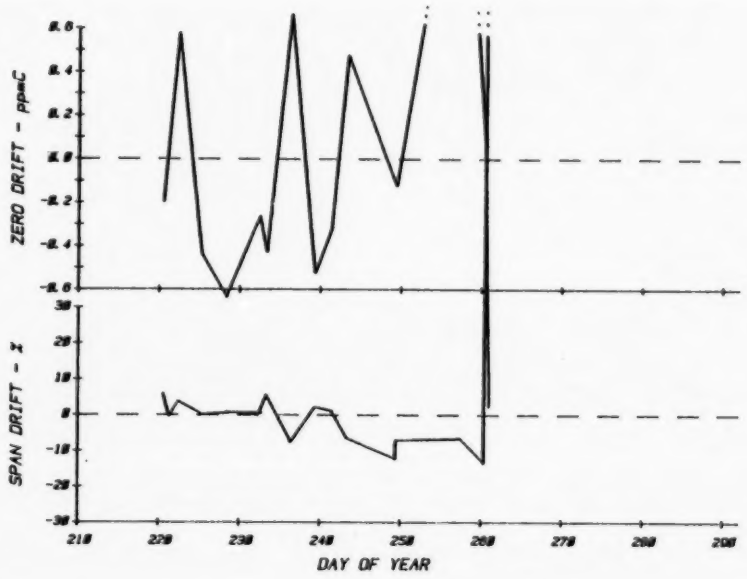


Figure 14. Baseline 1030-A cumulative zero and span drift.

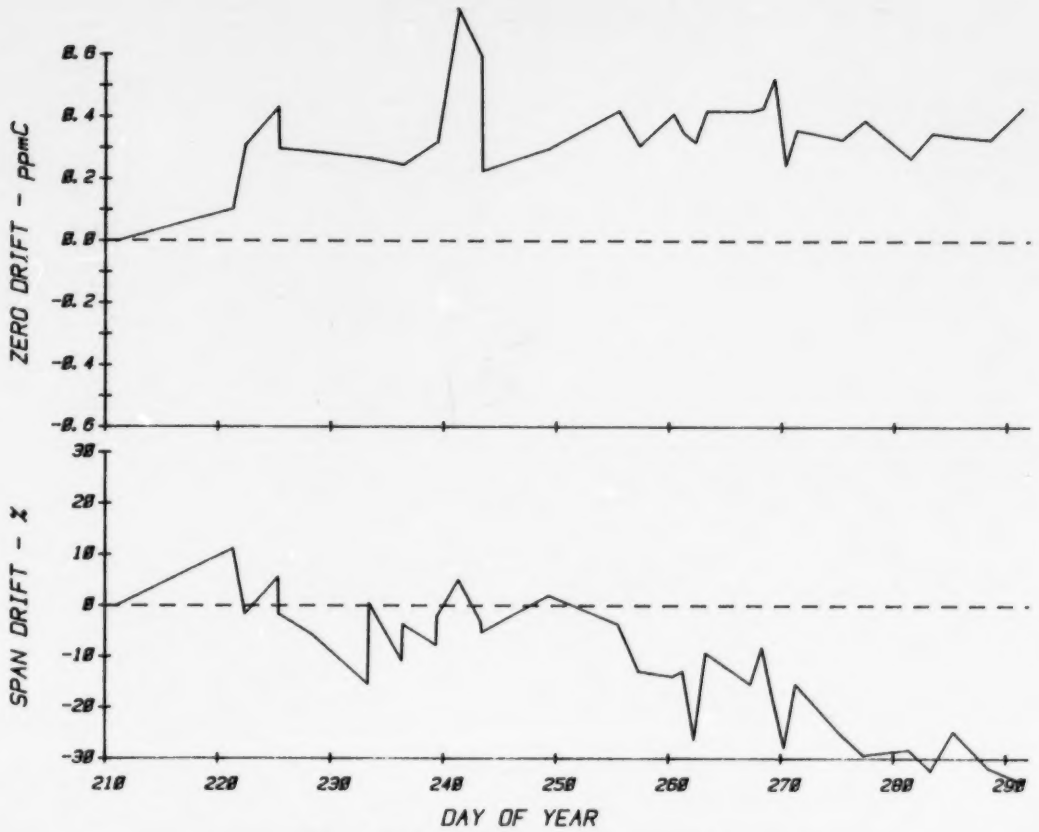


Figure 15. HNU PI 201 cumulative zero and span drift.

FID SENSITIVITY EVALUATION

Comparison of Two FIDs

It is well known that the response of an FID varies among different organic compounds. It has also been documented that the response pattern to various organic compounds apparently varies from one FID to another. To further investigate these phenomena, two different FIDs were tested with 10 different organic compounds representing paraffins, olefins, ketones, and aromatics. The compounds are identified and their respective FID responses are shown in Figure 16.

The FIDs used in this test were those in the MSA and the Bendix analyzers (only one of the MSA's two identical FIDs was used). The analyzers were operated so that the test compounds were routed directly to the FID (TOC mode of operation). The MSA and Bendix FIDs are different in physical design, but the manufacturer's recommended hydrogen-to-sample flow rate ratios ($\cong 1.0$) for both analyzers are approximately the same.

The ppmC responses shown in Figure 16 are all plotted relative to the ppmC response to propane, which was arbitrarily set to 100. Isopentane produced the greatest response, and the response to methane was about 30 percent greater than that for propane. Interestingly, the response of the two FIDs was equal or nearly equal for the paraffins, isobutylene, and ethylene. Some differences between responses from the two FIDs appear for propylene and aromatics, although the differences are not large and do not seem to follow a readily discernible pattern. Figure 16 suggests the use of propane as a calibration standard because response to propane is approximately equal to the combined average response from the other NMOCs.

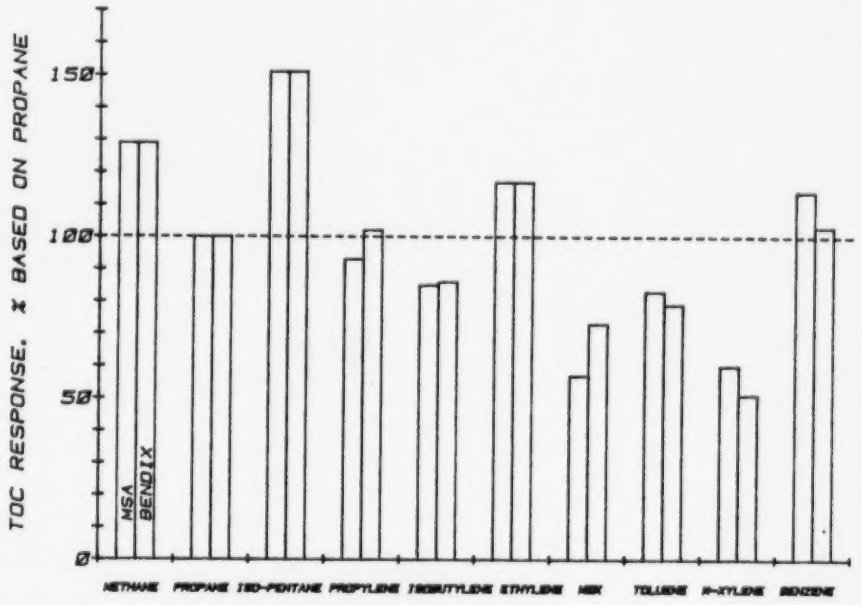


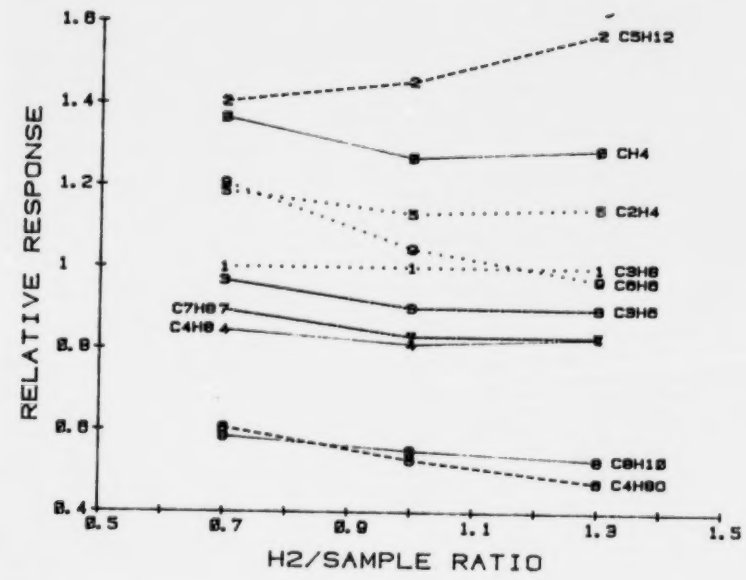
Figure 16. Comparison of relative TOC responses from two FIDs while sampling various organic compounds.

FID Sensitivity to Flow Changes

The comparison of the two FIDs was carried further to try to determine the extent to which the response patterns illustrated in Figure 16 changed with changes in the hydrogen-to-sample flow ratio and in the burner air (blanket air) flow rate. Responses to each of the organic compounds were obtained at various combinations of these variables. A randomized complete block design experiment with a factorial arrangement of two burner air flow rates and three hydrogen-to-sample flow ratios was used. Burner air flows of 300 cm^3/min (normal) and 172 cm^3/min were tested in the MSA and flows of 400 cm^3/min (normal) and 226 cm^3/min were tested in the Bendix. Hydrogen-to-sample flow ratios of 0.7, 1.0, and 1.3 were tested in the MSA and ratios of 0.9, 1.0, and 1.1 were tested in the Bendix. For both FIDs, a hydrogen-to-sample ratio of 1.0 was the normal, specified ratio. All flow conditions were obtained by adjustment of the analyzer's flow controls within their normal range. The hydrogen-to-sample ratios were initially adjusted to just above the flame-out conditions at 0.7 and 0.9 for the MSA and Bendix, respectively, and the upper ratios of 1.3 and 1.1 were selected to be symmetrical with respect to the normal ratios of 1.0.

The relative (propane=1) responses of the MSA and Bendix are shown in Figures 17 and 18, respectively. An analysis of variance showed that for the MSA analyzer, the hydrogen/sample ratio did have a statistically significant overall negative linear effect on analyzer response; i.e., an increase in the flow ratio produced a decrease in analyzer response. Also, an increase in burner flow rate produced a statistically significant linear increase in analyzer response. However, it is obvious from Figure 17 that these effects are mild and that minor changes in either the flow ratio or the burner air flow cause relatively minor changes in the FID response for most compounds tested.

For the Bendix analyzer, the various flow ratios did not have a statistically significant effect on analyzer response. But increasing the burner flow levels did produce a statistically significant linear increase in the FID response. Again, the changes were relatively minor for most of the tested compounds.



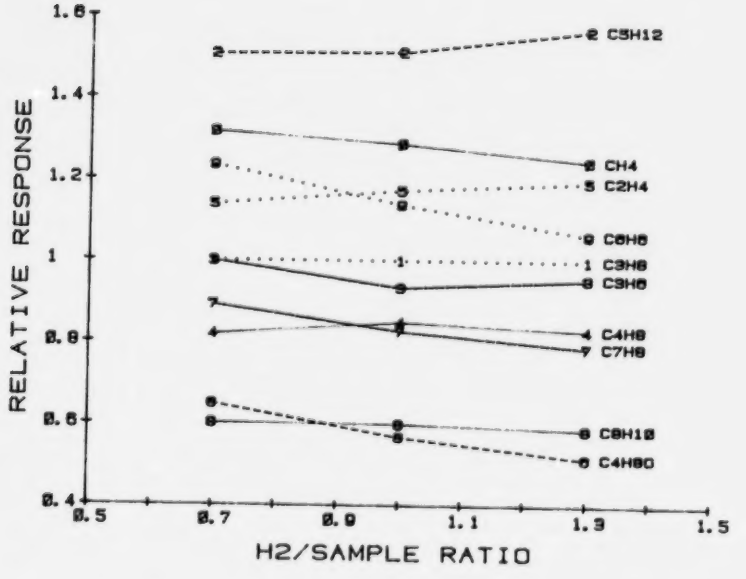
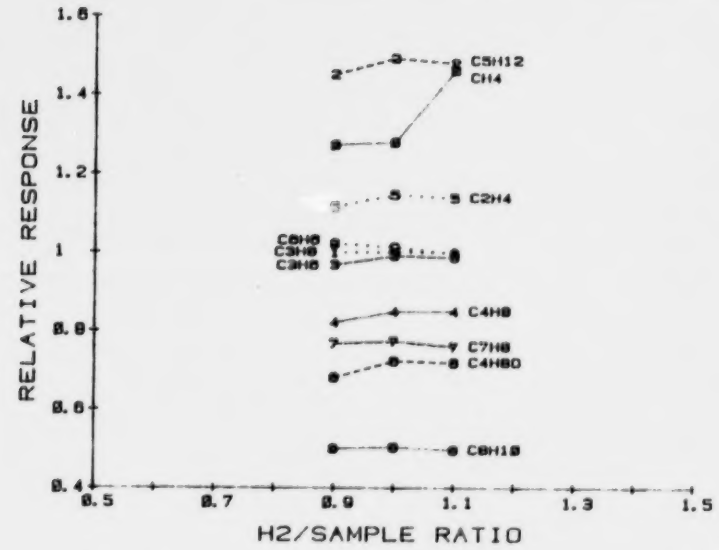


Figure 17. Effects of varying burner conditions in the MSA FID.



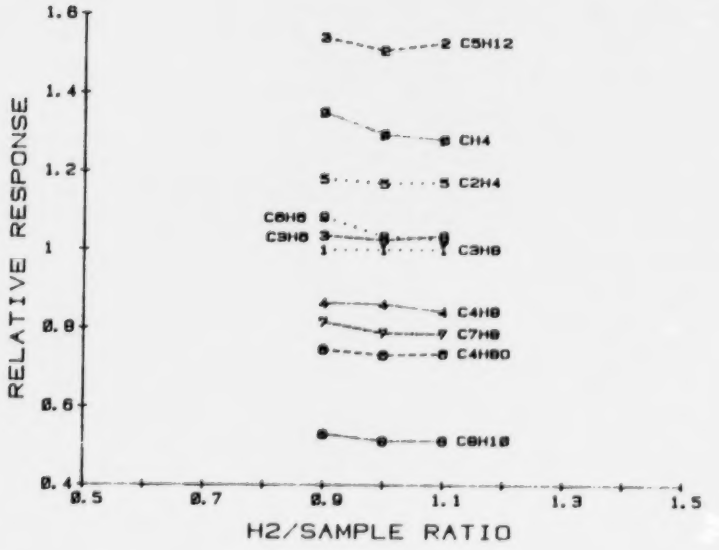


Figure 18. Effects of varying burner conditions in the Bendix FID.

FID Sensitivity to Oxygen Content

The FIDs in the MSA and the Bendix analyzers were also tested to determine their sensitivity to changes in the oxygen content of the sample air. Figure 19 shows the results of these tests. The highest data points shown represent the normal oxygen content of ambient air--about 21 percent. Because of the substantial sensitivity of the FIDs to changes in oxygen content, it is obviously important to ensure that calibration standards for FID analyzers prepared from cylinder standards have the correct oxygen content.

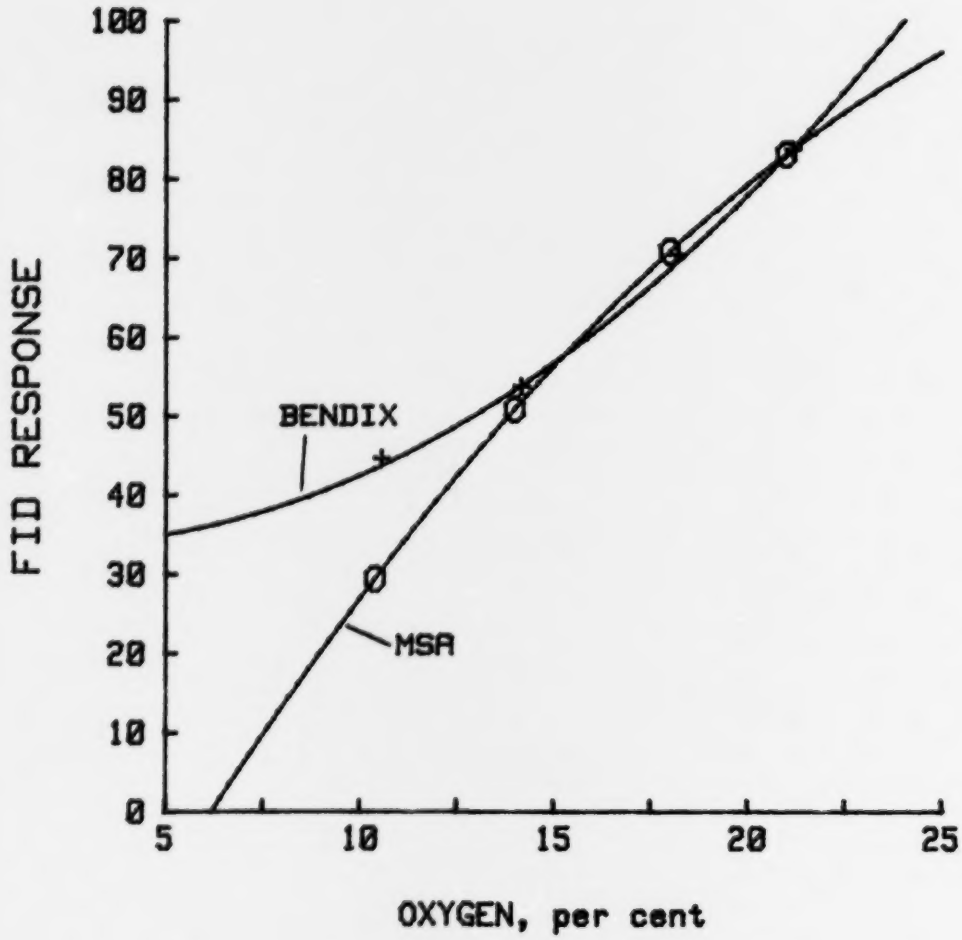


Figure 19. Response of Bendix and MSA FIDs to variations in oxygen content of samples.

COMPARISON OF ANALYZER RESPONSES TO SYNTHETIC HYDROCARBON SAMPLES

In another test, various mixtures of specific hydrocarbon compounds were introduced into a common manifold where they were sampled by all the test analyzers during normal operation. (At the time of this test, the Baseline analyzer had been withdrawn from the study.) The compounds were obtained from compressed gas cylinders and included mixtures of paraffins, aromatics, and olefins as indicated in Table 4. Concentrations of these compounds were verified twice by manual GC analysis. The cylinder concentrations were diluted with zero air to provide various concentrations within the 0 to 10 ppmC range of the analyzers. While the analyzers were sampling the synthetic atmospheres, bag samples were also taken from the common manifold for subsequent analysis by manual GC. The results of this test are shown in Figure 20. The bar heights for the paraffin, aromatic, and olefin responses are based on the least squares slope for several concentrations of each mixture.

TABLE 4. SYNTHETIC HYDROCARBON MIXTURES

Paraffin cylinder			
Ethane		124.2 ppmC	24.6%
Propane		143.3 ppmC	20.3%
Isobutane		118.9 ppmC	23.5%
Normal butane		119.2 ppmC	23.6%
	Total	505.6 ppmC	100.0%
Aromatic cylinder			
Toluene		48.5 ppmC	47.2%
Benzene		54.2 ppmC	52.8%
	Total	102.7 ppmC	100.0%
Olefin cylinder			
Ethylene		113.2 ppmC	27.8%
Propylene		133.7 ppmC	32.8%
Isobutylene		160.7 ppmC	39.4%
	Total	407.6 ppmC	100.0%

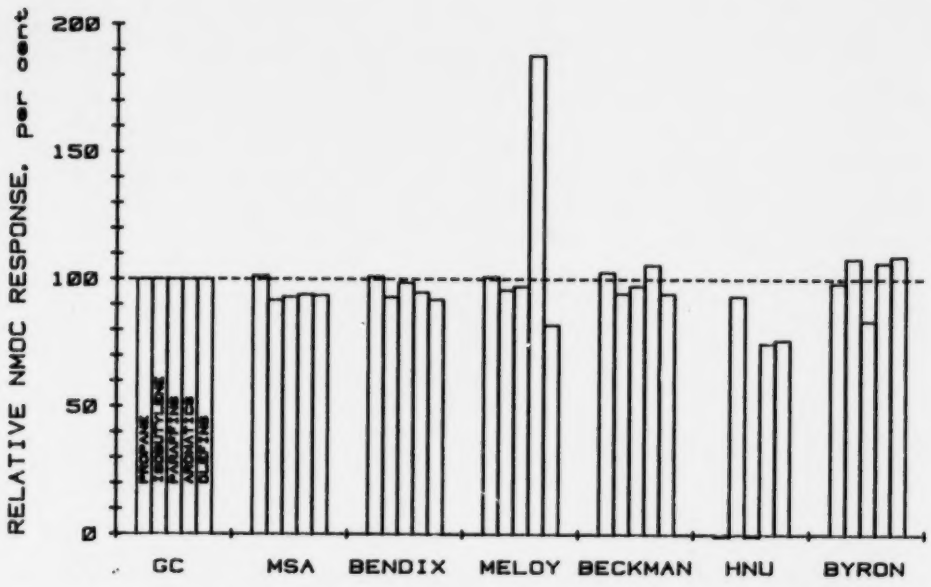


Figure 20. Comparison of the relative responses of the test analyzers for propane, isobutylene, and three NMOC mixtures, using the corresponding GC measurements as a reference. The responses are based on the least squares regression slope for several concentrations of each compound or mixture.

The responses of the four conventional analyzers (MSA, Bendix, Meloy, and Beckman) to the paraffin, aromatic, and olefin mixtures are rather similar, except for a slightly elevated response to aromatics by the Beckman and an exceptional response by the Meloy to the aromatics. We have no explanation for the Meloy's high response to aromatics and can only speculate that something about the absence of the concentric blanket air (burner air) surrounding the flame in the Meloy FID causes the exceptional aromatic sensitivity. The data of the other three conventional FID analyzers were also quite similar to that obtained from the manual GC analysis. This is significant because it reinforces both the selection of propane as a suitable calibration material (the analyzers were calibrated to propane standards) and the use of conventional FID analyzers as a surrogate for GC for measuring ambient NMOC.

The responses of the two nonconventional analyzers are generally dissimilar. The HNU showed no response to the propane or to the paraffin mixture. Response to the aromatics and olefins was about 20 percent less than the conventional analyzers. If the HNU were referenced to isobutylene instead of propane (i.e., not using the 0.85 factor--see page 18), its response would be only slightly below the response of the conventional FIDs for aromatics and olefins. The response of the Byron appears similar to that of the conventional FIDs and to the GC readings, but comparison of the ambient air readings shows less agreement and thus conflicts somewhat with these results (see next section).

COMPARISON OF CONVENTIONAL ANALYZER RESPONSES TO AMBIENT AIR SAMPLES

Sequential Plot of Hourly Readings

A chronological plot of the readings from the four conventional FID analyzers over the entire 82-day test period is shown in Figure 21. Instead of plotting individual hourly readings, the plots are smoothed by plotting 60-hour running averages. This removes fine detail and makes the plots easier to compare. (The factor of 60 was selected empirically to show the best comparison and has no other significance.) Supplemental propane at a concentration of 0.87 ppmC was added to the ambient air sample from 1400 hours on October 8 (day 281) to 800 hours on October 10 (day 283). No other pollutant augmentation was used. The relatively high ambient NMOC concentrations noted during the final days of the test period are typical of the characteristic autumnal increase in NMOC concentrations at the Durham, NC, test site.

Figure 21 shows that the analyzers agreed fairly well during the last part of the period, but agreed poorly prior to day 250. In particular, the Bendix analyzer produced negative readings at times prior to day 247, and many data were missing for the Meloy, MSA, and Beckman during this period. As noted earlier, many analyzers experienced startup and operational problems during the early part of the study. The Beckman had unstable performance and numerous flame-out problems prior to replacement of a valve on day 250. Timing and flow misadjustments on the Bendix (discovered and corrected on day 248) caused low response to higher hydrocarbons and was apparently responsible for the negative readings prior to day 248. The MSA was plagued with minor malfunctions and moisture problems until about day 264, and the Meloy was erratic during much of the period but had particularly severe problems until day 235.

If we consider only the period from day 252 until the end of the study on day 292, the analyzers show better agreement, as shown in Figure 22. This figure shows that the Meloy read consistently high, which may have been due, at least in part, to its extra high sensitivity to aromatics (see Figure 20). Also, the Meloy analyzer had a much higher ratio of methane to propane per carbon response than the 1.3 ratio characteristic of the other conventional analyzers. Perhaps these phenomena are related to the unique burner design of the Meloy FID. Considering only the remaining three conventional analyzers and the day 252-292 period, the agreement is good, as shown in Figure 23. More quantitative comparisons follow.

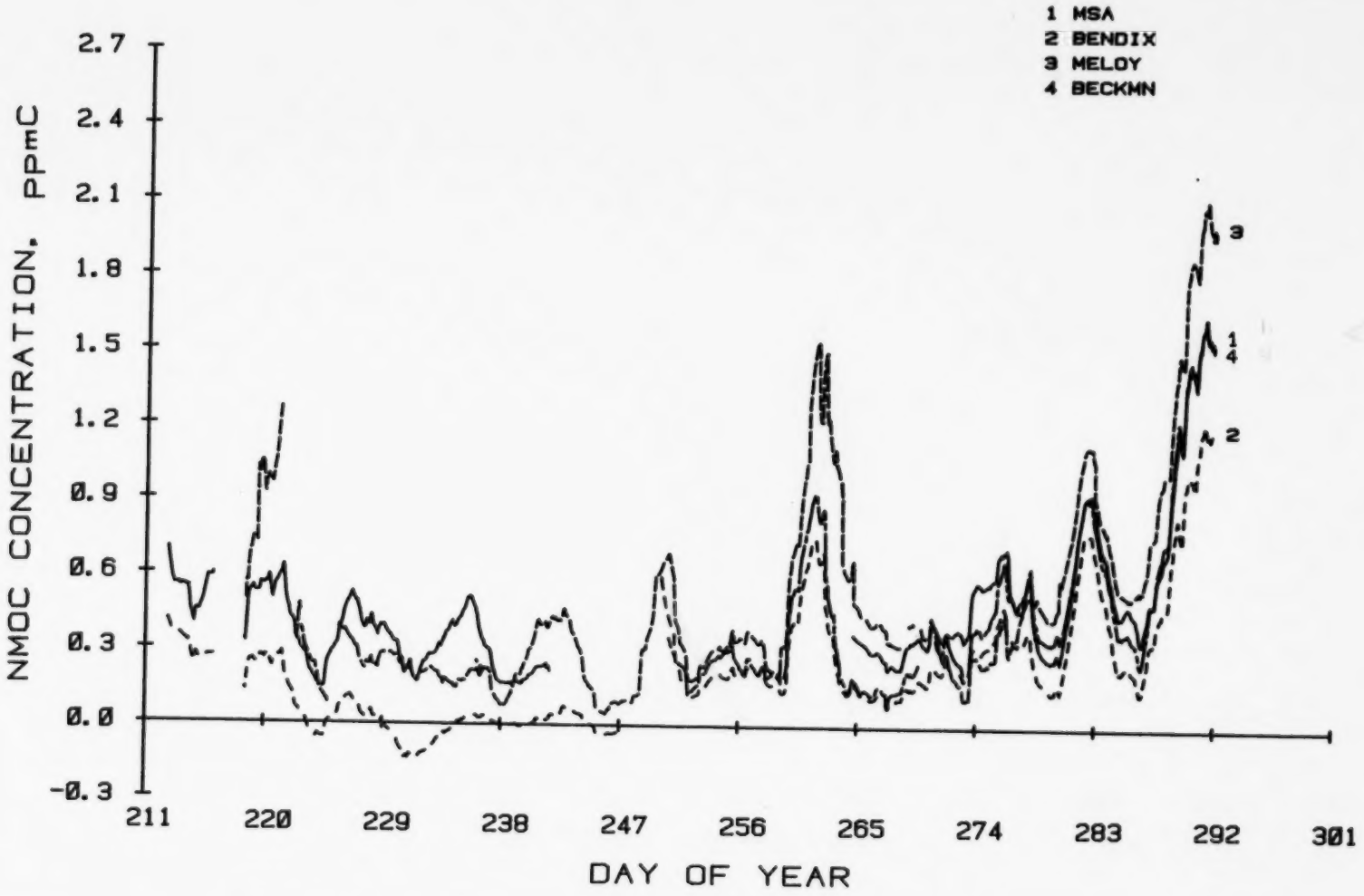


Figure 21. Sequential plot of ambient air NMOC measurements from four conventional analyzers during days 211 to 292 (60-hour running averages).

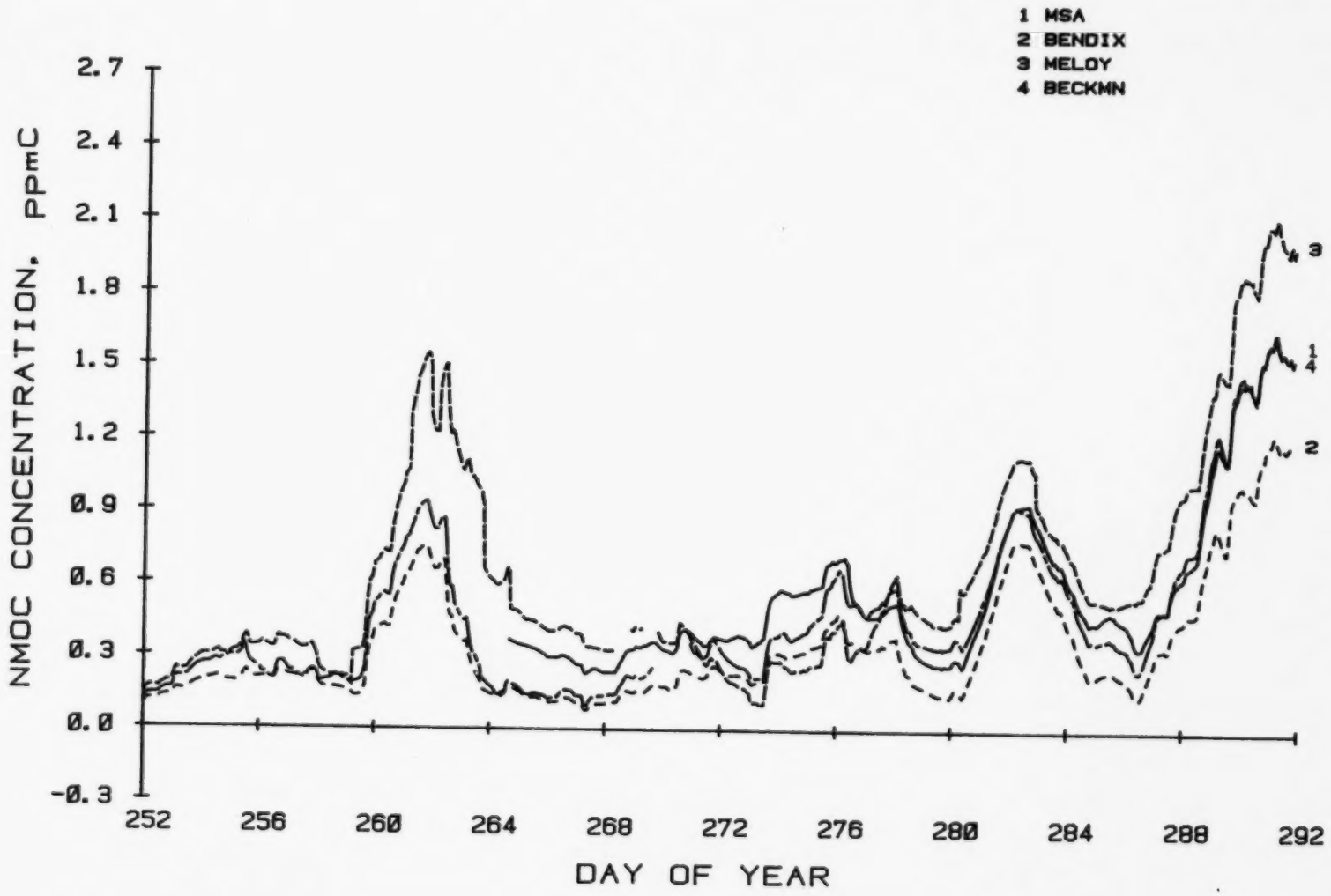


Figure 22. Sequential plot of ambient air NMOC measurements from four conventional analyzers during days 252 to 292 (60-hour running averages).

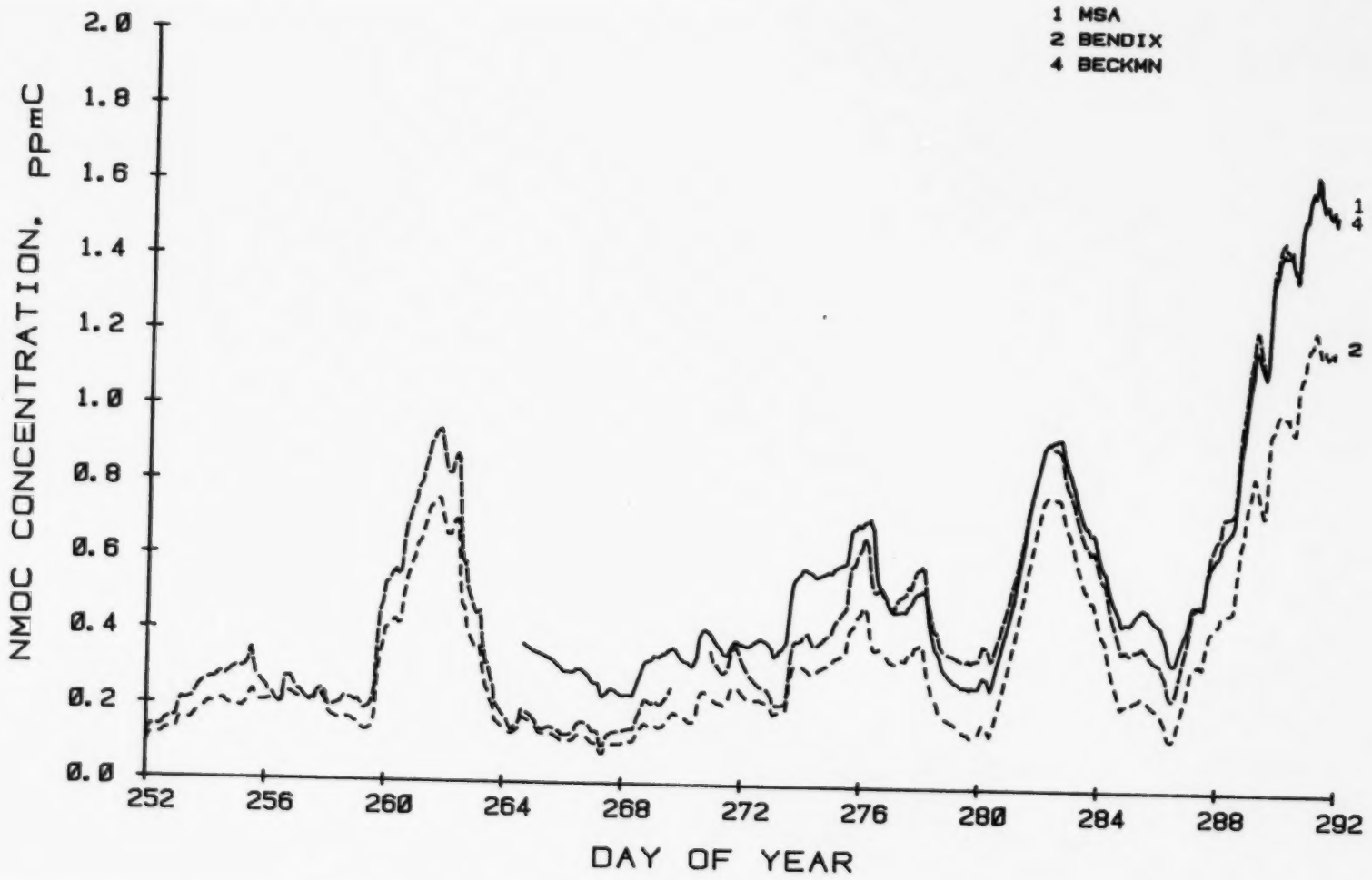


Figure 23. Sequential plot of ambient air NMOC measurements from the MSA, Bendix, and Beckman analyzers during days 252 to 292 (60-hour running average).

Intercomparison of Automated Analyzers

Quantitative comparisons between simultaneous hourly averages of the Bendix and MSA conventional analyzers are shown in Figure 24. The upper part of the figure shows a scatter plot of the hourly averages for the full test period (days 211-292); the lower plot covers the day 252-292 period during which the analyzers appeared to be operating properly. Shown on these figures is the orthogonal slope (M), intercept (A), and correlation (r). The orthogonal statistics (8) are similar to ordinary least-squares regression statistics. However, least-squares regression assumes that one of the variables is dependent on the other variable, that the independent variable has zero measurement error, and that all of the variance (scatter) in the data points must be due to the variance in the dependent variable. Since this is not the case when comparing two independent analyzers, the balanced orthogonal analysis, which assumes equal measurement error in both variables, has been used.

Comparing the two diagrams in Figure 24, we see improvement in going from the full period to the period between days 252 and 292. As expected from looking at Figures 21 and 22, most of the negative Bendix readings were eliminated. The slope and intercept improve somewhat, and the correlation improves considerably. Also, the difference between the averages decreases from 0.248 to 0.201 ppmC. Similar improvement can be shown for the other five possible analyzer-pair combinations for the four conventional analyzers. Thus, Figures 21 and 22 and the example shown in Figure 24 serve to adequately justify the use of the limited period (days 252-292) for subsequent analysis of the conventional analyzer data.

Figure 24 also illustrates how the ambient readings are heavily clustered in the low concentration region of the scale (as is typical of ambient pollutant data). A more appropriate analysis of the data is obtained if the data are transformed logarithmically. This transformation spreads the measurements more evenly across the concentration range of the data and reduces the otherwise excessive effect of high concentration points. Thus, the logarithmic transformation stabilizes the error variance and improves the normality assumptions of the linear model (see Reference 9).

The linear model shown in equation 2 was fitted to the transformed data, assuming each analyzer to have equal measurement errors (orthogonal analysis).

$$\ln(y+1) = \alpha + \beta \ln(X+1) + \text{error} \qquad (2)$$

A constant value of one was added to each measurement to eliminate all negative values. If the methods are equivalent, the slope should equal one and the intercept should equal zero. Scatter diagrams for the transformed data are shown in Figures 25 through 30.

Comparing the Bendix and MSA analyzers (Figure 25), the correlation coefficient of 0.97 is quite good but the intercept (-0.13) indicates that

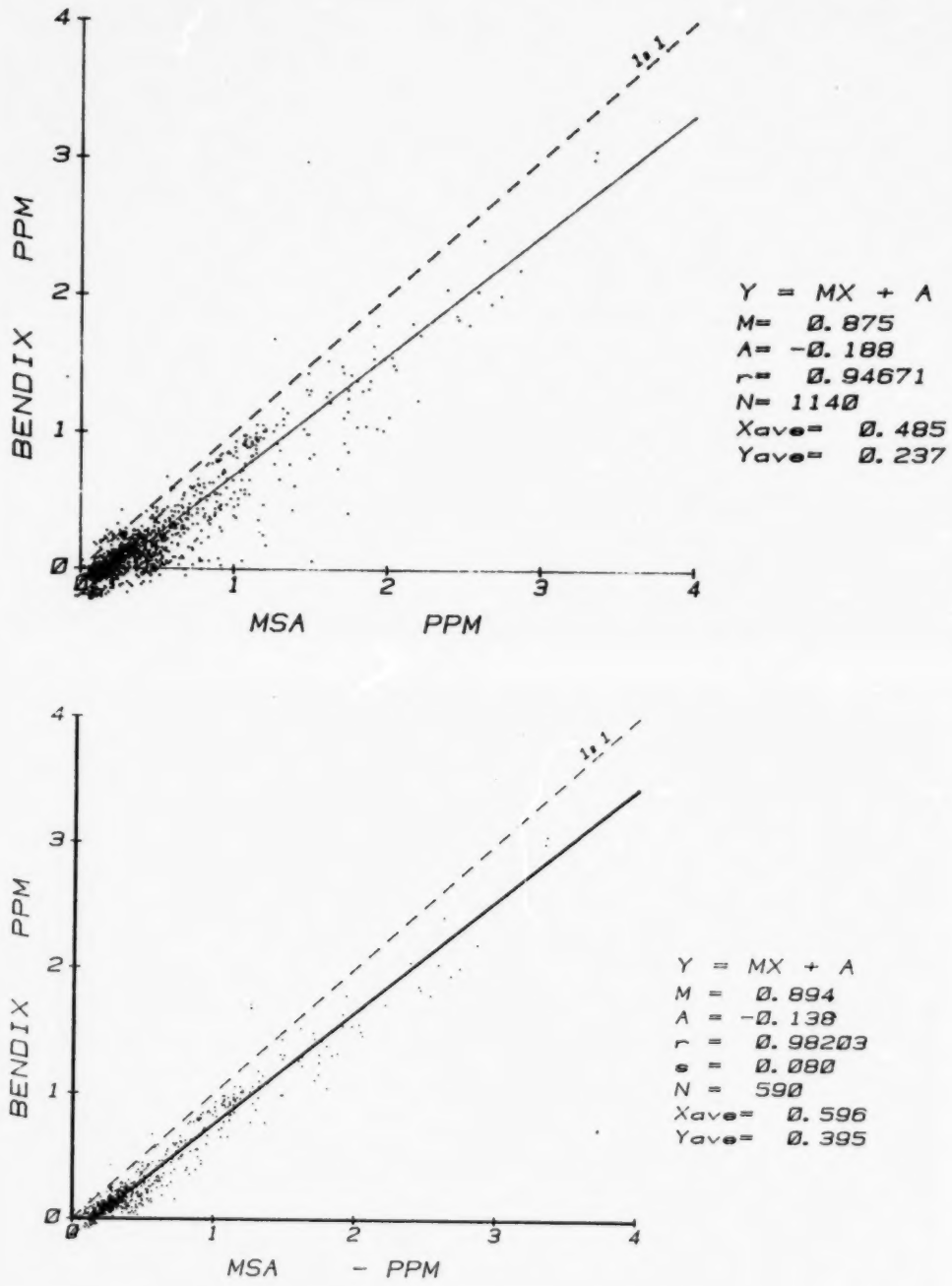


Figure 24. Comparison of ambient air NMOC measurements from the complete and limited data sets (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation).

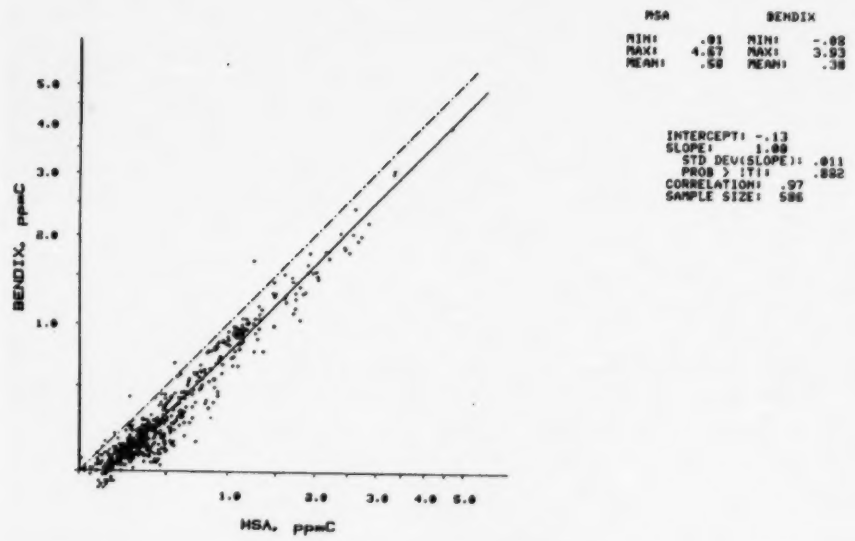


Figure 25. Comparison of transformed ambient air NMOC measurements from the MSA and Bendix (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation).

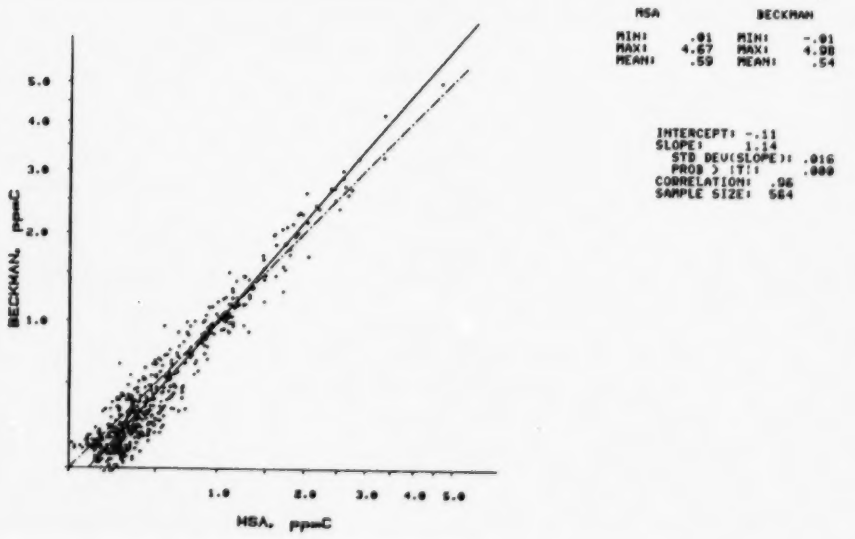


Figure 26. Comparison of transformed ambient air NMOC measurements from the MSA and Beckman (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation).

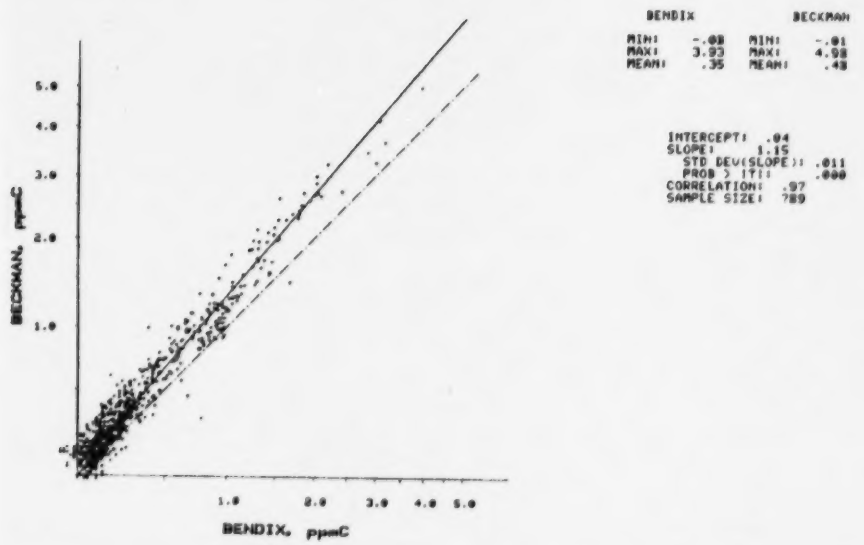


Figure 27. Comparison of transformed ambient air NMOC measurements from the Bendix and Beckman (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation).

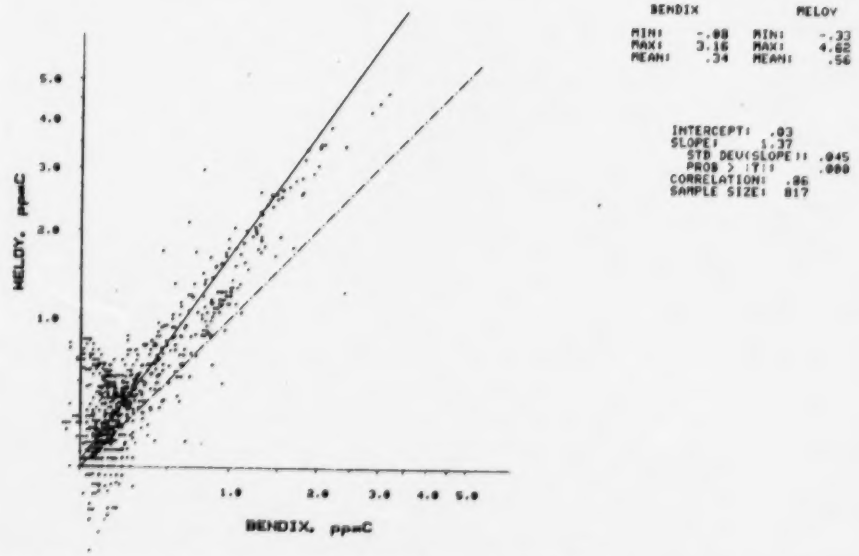


Figure 28. Comparison of transformed ambient air NMOC measurements from the Bendix and Meloy (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation).

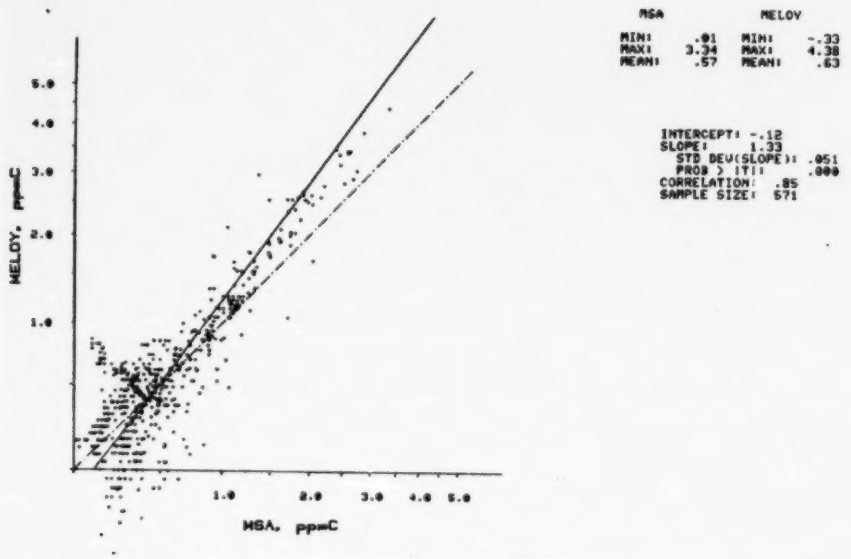


Figure 29. Comparison of transformed ambient air NMOC measurements from the MSA and Meloy (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation).

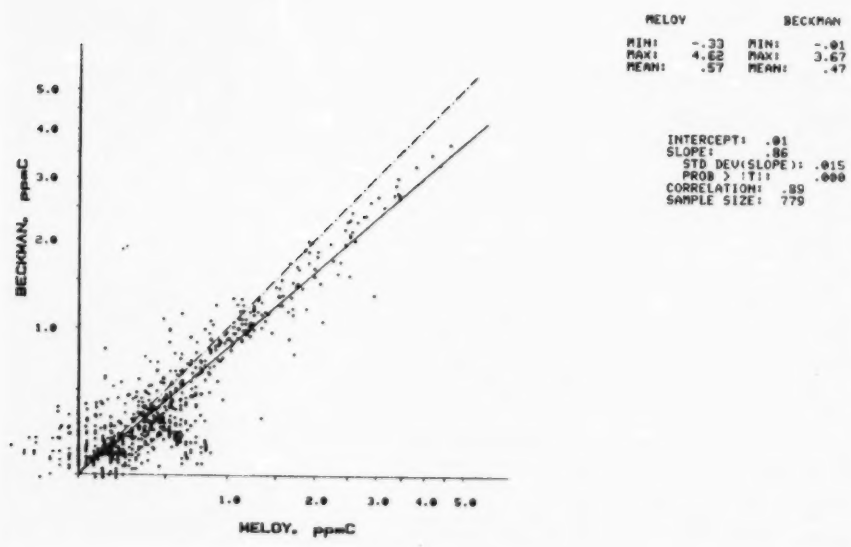


Figure 30. Comparison of transformed ambient air NMOC measurements from the Meloy and Beckman (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation).

the Bendix reads characteristically lower than the MSA.* The difference in the analyzers' averages for the 586 hourly measurements shows that the Bendix reads 0.20 ppmC lower than the MSA.

The Beckman and MSA analyzers appear to have the best agreement, as shown in Figure 26. Although the correlation of 0.96 was not the highest of the six analyzer pairs, it is quite good. Also, the difference in the analyzers' averages for the 564 hourly measurements is only 0.05 ppmC. This is due to a combination of the slope being greater than 1 (1.14) and the intercept being less than zero (-0.11), which results in a correlation line that crosses over the 1=1 line.

In Figure 27, the Beckman-Bendix comparison shows a high correlation (0.97) and low intercept (0.04), but the Bendix reads characteristically lower than the Beckman. The difference in the averages for the 789 hourly measurements shows that the Bendix reads 0.13 ppmC lower than the Beckman.

The Meloy analyzer is compared to the MSA, Bendix, and Beckman analyzers in Figures 28, 29, and 30. Here we see considerably greater scatter (variability) and lower correlations. In addition, the Meloy reads characteristically higher than the other three analyzers (also indicated by Figure 21).

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* It could just as well be said that the MSA reads characteristically higher than the Bendix, since neither analyzer is considered a reference nor has one more credibility than the other. Similarly, whether an analyzer's data are plotted along the ordinate or abscissa in Figures 25 through 30 has no significance.

Determination of Minimum Detection Limit

Of particular interest for any air monitoring analyzer is its minimum measurement capability. In an effort to determine the lower sensitivity limit of each analyzer, a confidence interval was constructed around zero, using the unbiased estimate of the residuals' variance of a multivariate model. This approach is based on defining the minimum detection limit at a point where an analyzer can distinguish a finite amount of NMOC from zero. This interval will contain the true value, defined as zero in this case, 90 percent of the time for all future observations.

The statistical approach used assumes that each analyzer measurement is a measure of the true amount of NMOC in the ambient air at a given time. Using principal components analysis (see Reference 10), a multivariate model can be constructed that predicts a measurement from the estimated true NMOC concentration. Using this approach, estimates of the minimum detection limit for the four analyzers are listed in Table 5.

TABLE 5. ESTIMATES OF MINIMUM DETECTION LIMITS

Analyzer	MDL (ppmC)
MSA	0.13
Bendix	0.12
Beckman	0.10
Meloy	0.32

It should be noted that these estimates of lower sensitivity limits do not include errors associated with other operators and laboratories. Thus, these estimates are probably lower than what would be determined if other variables were included. Note that the estimate is considerably larger for the Meloy than for the other three analyzers.

Automated Analyzers Versus Manual GC

An important objective of the study was to compare the automated analyzer's measurements to measurements by sum-of-species gas chromatography with flame ionization detection (hereafter referred to as manual GC; details of this test are given in Section 3). Basically, the test involved collecting a portion of the ambient sample in Tedlar bags for analysis by the manual GC. Bag samples were obtained in October 1979 on days 276, 282, 284, 289, and 290. All of these days are within the period when the analyzers were presumed to be operating properly (days 252 to 292). During the test, 3-hour composite bag samples were taken on days 276, 282, and 284 and 1-hour bag samples were taken on days 289 and 290. In all, 48 bag samples were obtained. On day 282, the ambient sample was augmented with approximately 0.87 ppmC propane. Thus eight bags contained ambient air "spiked" with propane.

Comparisons between the manual GC analyses and the conventional NMOC analyzers are shown in Figures 31, 32, 33, and 34. The upper portion of each figure shows the scatter diagram, and again the data have been logarithmically transformed for the same reasons given earlier.

The propane-augmented samples are indicated by a "+". In this case, quantitative comparison is provided by conventional least-squares regression analysis on the assumption that the manual GC analysis can be considered the "true" analysis; i.e., that there is zero measurement error in the GC analysis. Although there is certainly some degree of measurement error in the GC analyses, the error is believed to be smaller than that for the continuous analyzers, hence the GC can be used here as a reference.

Correlation coefficients are in the range of 0.96 to 0.97 except for the Meloy analyzer, which, as noted previously, was more erratic than the other three analyzers. Based on t-tests, the MSA slope (1.061) was not different from 1.000 at the 95 percent significance level. The slopes for the other analyzers were different from 1.000 at the 95 percent level, indicating a proportional difference ranging from about +12 percent (for the Bendix) to about +18-19 percent (Beckman and Meloy). The intercepts of the Beckman (-0.01) and Meloy (+0.097) were not different from 0 at the 95 percent significance level, but the MSA (0.079) and Bendix (-0.125) intercepts were significant, indicating a constant difference for the latter two analyzers. Based on the averages for the 48 measurements, the Bendix was 0.082 ppmC lower than the GC, while the MSA, Beckman, and Meloy were higher by 0.226, 0.214, and 0.446 ppmC, respectively.

The lower portions of Figures 31 through 34 show corresponding frequency distributions of the actual (untransformed) differences between the analyzer readings. These distributions show that most of the actual discrepancies are within a few tenths of a ppmC. However, this may be somewhat misleading when obtaining NMOC data for use with an EKMA model because the higher NMOC readings are likely to be used as input to the model.

It is of interest to see what the results would have been if the analyzers had been calibrated with methane instead of propane. Figure 16 illustrates that the methane response of the MSA and Bendix analyzers is identical and equal to about 1.29 times the propane response. Thus, if the net responses of these analyzers were reduced by a factor of 0.775 (i.e., 1/1.29), the analyzers' calibrations would be referenced to methane instead of propane. Figures 35 and 36 show the comparisons of the MSA and Bendix based on calibration with methane.

Comparing Figures 35 and 31, we see that with calibration based on methane, the MSA slope is lower and is different from 1.000 at the 95 percent significance level, indicating a proportional difference of about -7 percent. The intercept is lower but still different from 0, indicating a constant difference of 0.042 ppmC. The averages are very close, differing by only 0.002. For the Bendix analyzer, methane calibration would have produced results similar to Figure 36, which can be compared to Figure 32. A t-test shows the Bendix's slope became indistinguishable from 1.000 at the 95 percent significance level, and the constant difference represented by

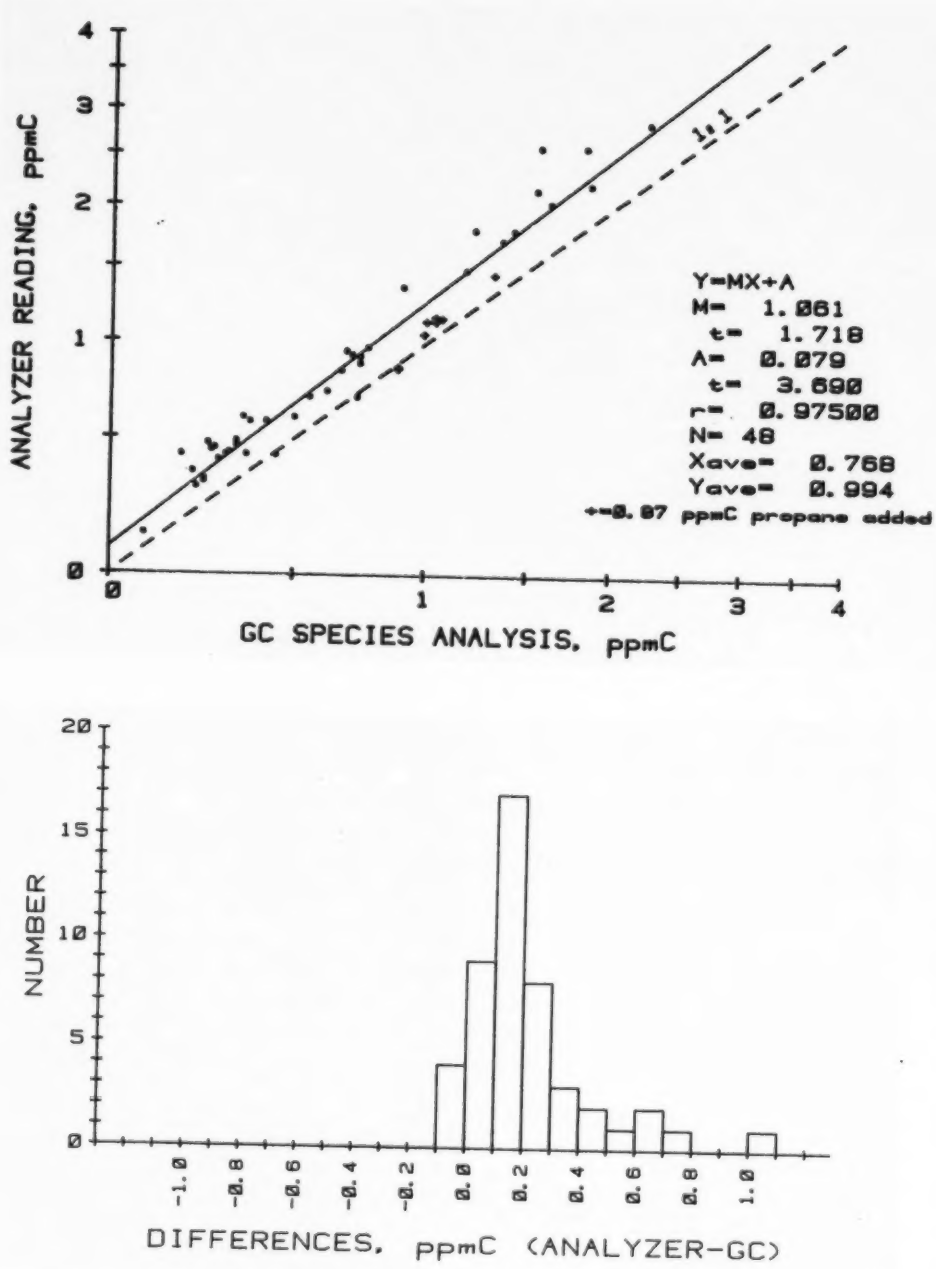

Figure 31. Comparison of ambient air NMOC measurements from the MSA and manual GC.

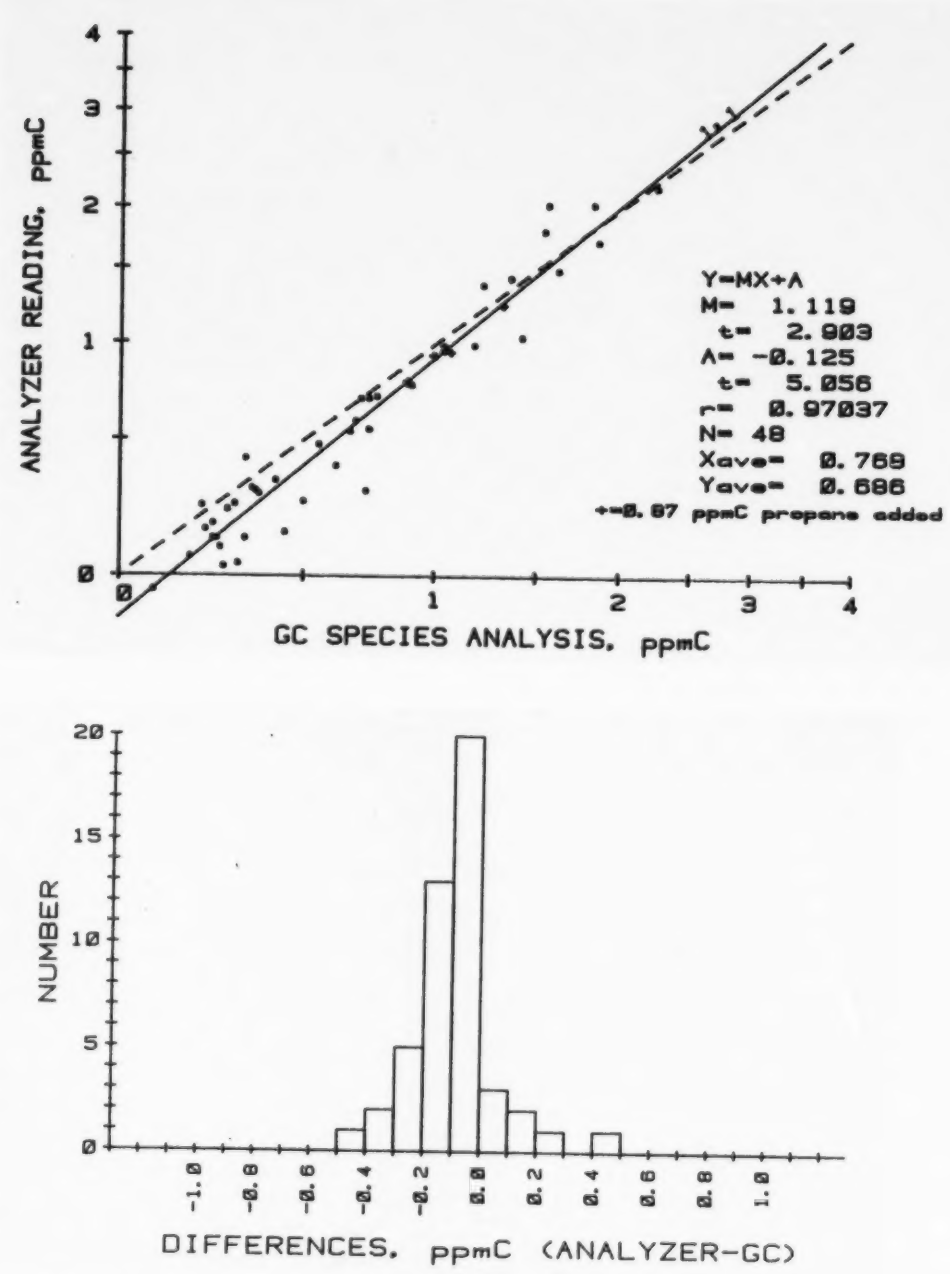

Figure 32. Comparison of ambient air NMOC measurements from the Bendix and manual GC.

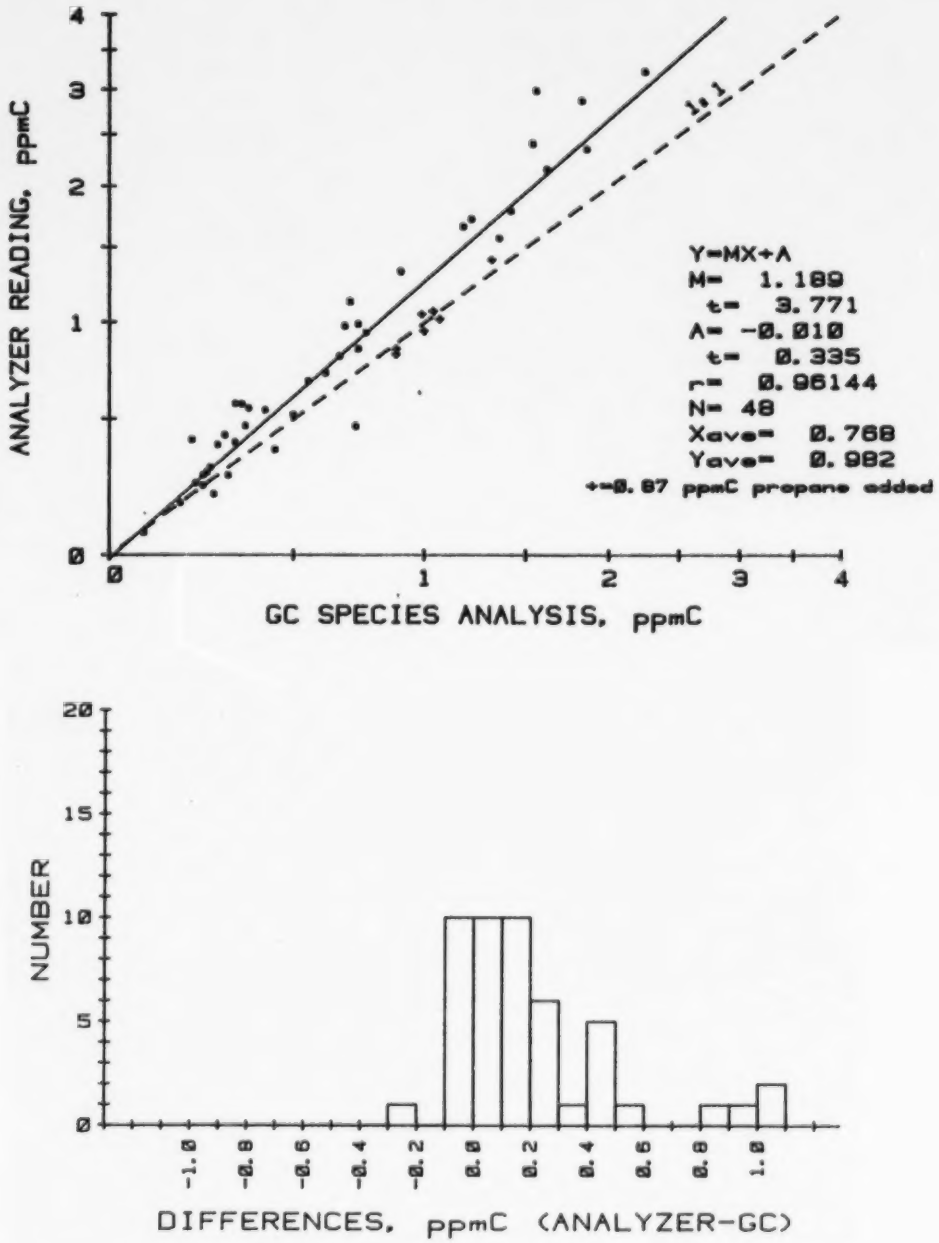

Figure 33. Comparison of ambient air NMOC measurements from the Beckman and manual GC.

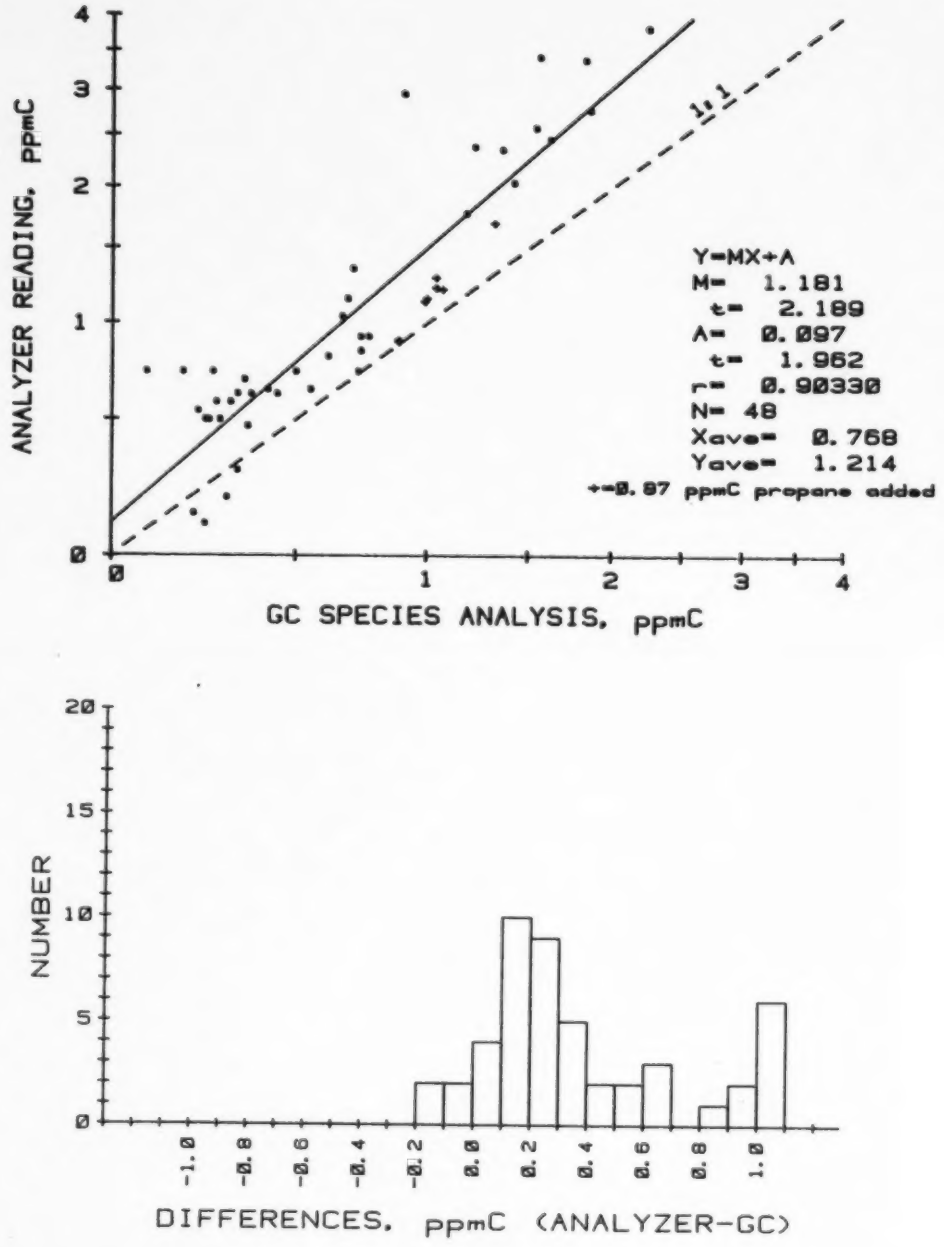

Figure 34. Comparison of ambient air NMOC measurements from the Meloy and manual GC.

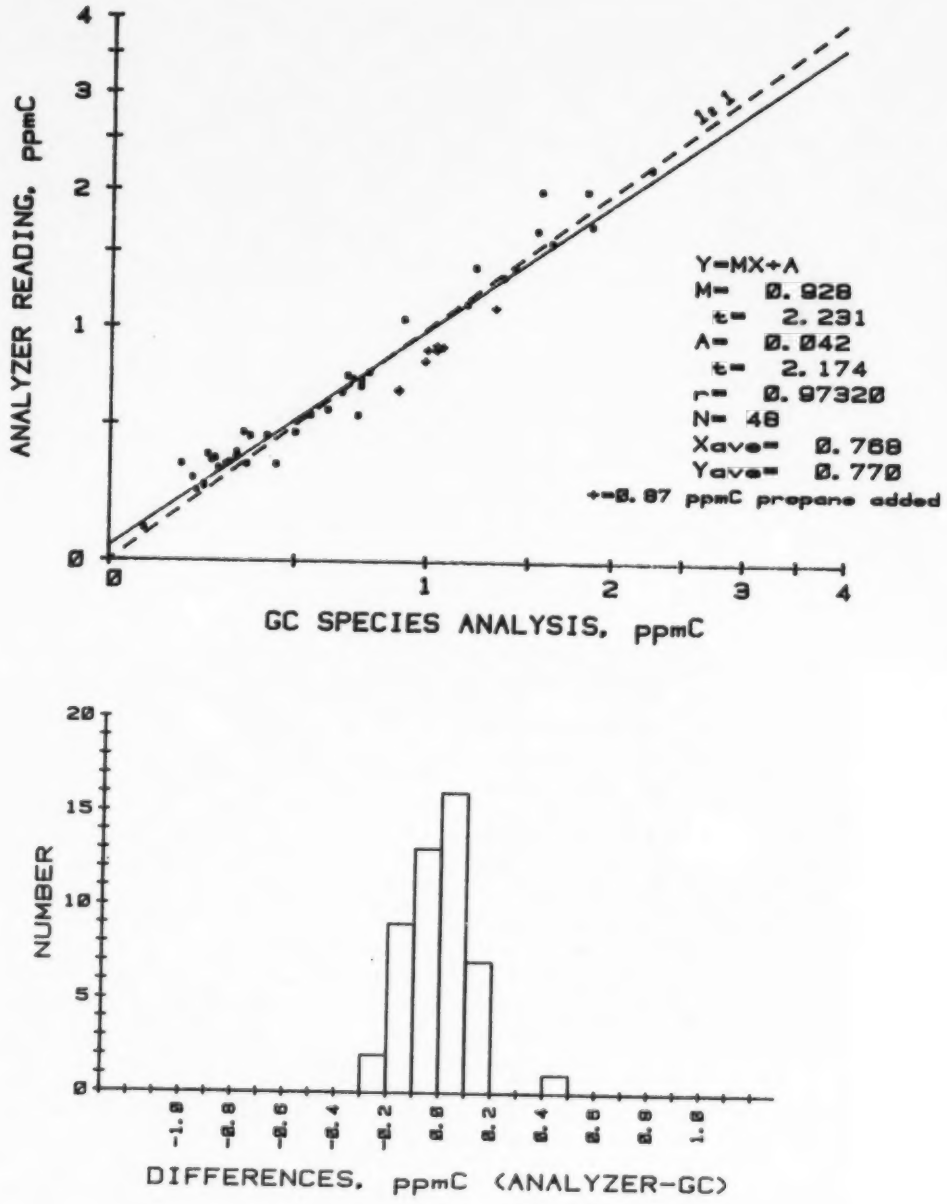

Figure 35. Comparison of ambient air NMOC measurements of the manual GC-FID and the MSA if the MSA had been calibrated with methane.

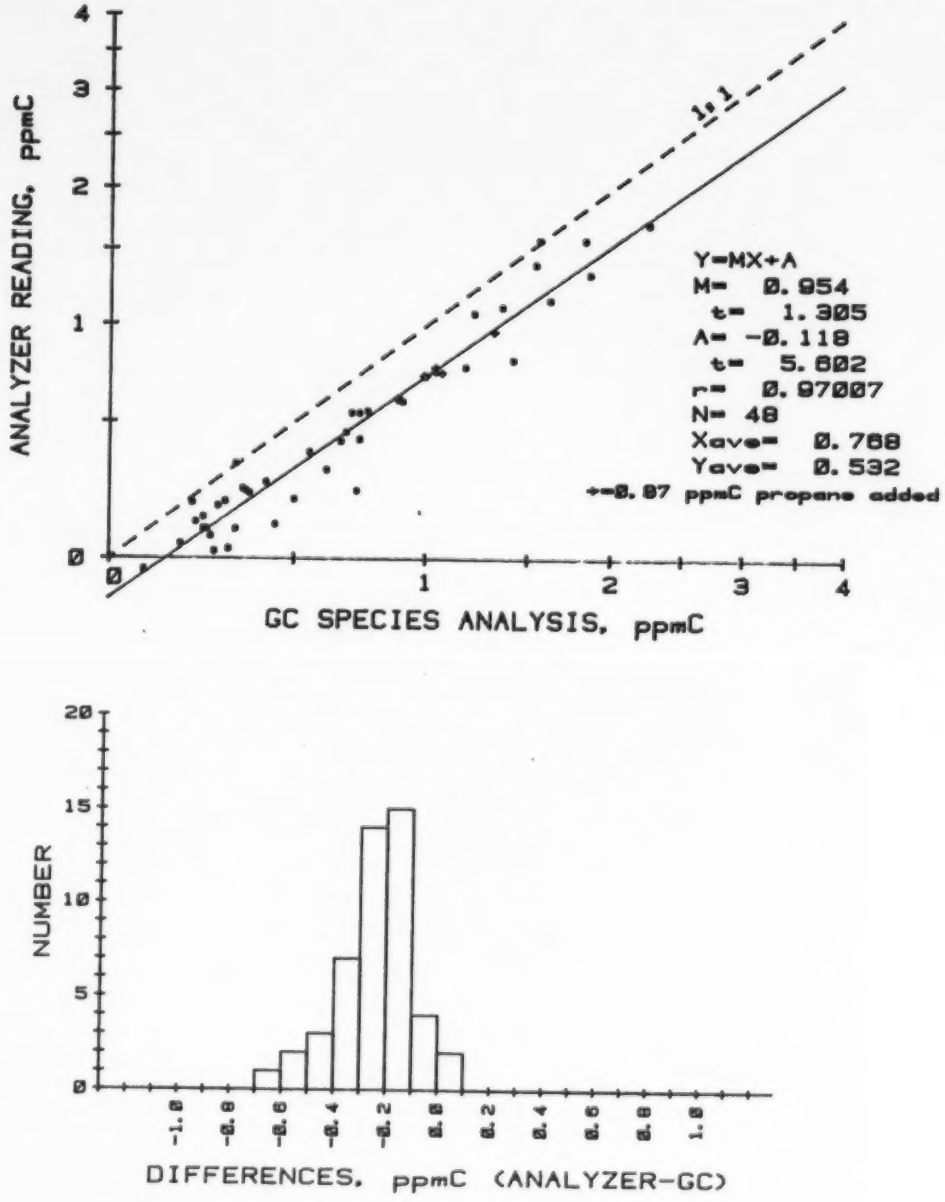

Figure 36. Comparison of ambient air NMOC measurements of the manual GC-FID and the Bendix if the Bendix had been calibrated with methane.

the intercept was still significant at -0.118 ppmC. This caused the Bendix average to be 0.236 ppmC lower than the GC measurements.

Figures 25 through 36 indicate that the differences between methane and propane calibration for the MSA and Bendix analyzers are generally comparable (i.e., of similar general nature and order of magnitude) to the differences observed among the four conventional analyzers. This information does not support the selection of propane rather than methane for calibration of NMOC analyzers and must be regarded as inconclusive in selecting either methane or propane over the other. Apparently either compound could be considered acceptable for calibration. Nevertheless, we believe calibration based on propane is preferable for the following reasons.

1. Propane is one of the compounds that the NMOC measurements are to include; methane is not.

2. Figure 16 clearly indicates that typical FID response to methane is higher than response to many, if not most, other hydrocarbon compounds, while propane appears to be more representative of the average response of such compounds.

3. As shown in Figure 20, propane calibration provided good agreement between most NMOC analyzers tested and the GC analyses for several various compound mixtures prepared in the laboratory.

4. Propane is more representative of the hydrocarbon mix used to calibrate the hydrocarbon analyzers that collected the data base from which the EKMA model was developed.

5. Direct-reading automated analyzers (which do not produce a CH_4 or TOC measurement) cannot be calibrated with methane and are generally calibrated with propane standards.

For the foregoing reasons, it is recommended that continuous NMOC data, obtained for use in dispersion models for predicting ozone concentrations, should be referenced to propane standards. CH_4 and TOC responses should continue to be balanced with, and referenced to, methane-in-air standards.

COMPARISON OF NONCONVENTIONAL ANALYZER RESPONSES TO AMBIENT AIR SAMPLES

Sequential Plot of Hourly Readings

The performance of the three nonconventional analyzers (HNU, Byron, and Baseline) was markedly different than that of the conventional analyzers. To illustrate the differences, ambient readings are compared in Figure 37. Contained in this figure are sequential plots of the hourly readings from the three nonconventional analyzers. Also contained in this figure is the plot from a representative conventional analyzer (MSA). Readings from each analyzer are smoothed by plotting 60-hour running averages, as was done in Figures 20 through 22. This effectively removes the fine detail and enables a clearer visual comparison.

Examination of Figure 37 points out the erratic response from the Baseline analyzer. As mentioned previously, this analyzer did not produce a linear calibration curve (see Figure 6). Furthermore, the Baseline's response to zero air standards was very erratic (see Figure 14). For these reasons, the Baseline analyzer was withdrawn from the study on day 261, and no further processing of its data was attempted.

Responses of the HNU and the Byron appeared to follow the trends of increasing and decreasing concentrations; however, the responses were seldom close to the representative conventional analyzer. Figure 37 shows the Byron measurements to be always higher than the MSA, whereas the HNU measurements are usually lower than the MSA.

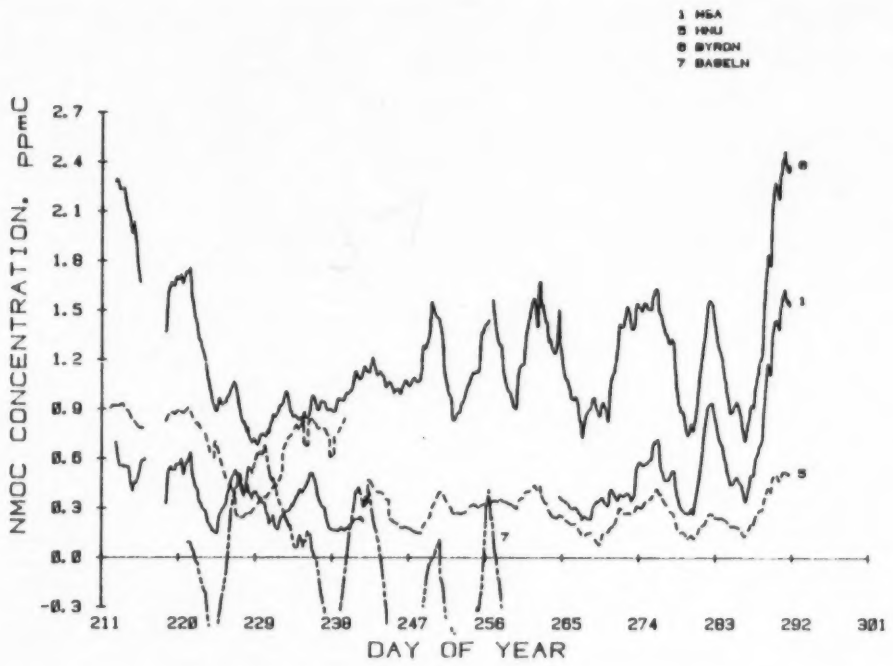

Figure 37. Sequential plot of ambient air NMOC measurements from the three nonconventional analyzers and the conventional MSA analyzer (60-hour running average).

Nonconventional Analyzers Versus Manual GC

Quantitative comparisons of the nonconventional analyzers to manual GC-FID are illustrated in Figures 38, 39, and 40. In these figures, the analyzers' logarithmically transformed NMOC measurements of ambient air are plotted against the manual GC measurements (see Section 3 for details on the ambient test). Least squares linear regression is used to quantify the relationship and compute the slope and intercept of the correlation curve, similar to Figures 31 through 34.

In Figure 38, the HNU's readings are substantially less than the manual GC-FID. Since the HNU does ot respond to ethane, propane and other low-molecular weight paraffins, the reduced response is expected. By eliminating the propane-spiked samples, the correlation, illustrated in Figure 39, is somewhat improved; however, the analyzer's response is still much less than that of the GC. In both cases, t-tests indicate that the slopes are significantly different than 1.000 and the intercepts are significantly different than 0 at the 95 percent level, indicating a substantial proportional error and a moderate constant error.

In Figure 40, the Byron's readings are shown to be considerably higher than the manual GC-FID. Although the slope is not different from 1.000 at the 95 percent significance level and correlation is 0.94, the clearly significant intercept of 0.413 ppmC indicates a large constant error, which is of particular concern as is the high intercept the analyzer exhibits. As noted in the comments section, column contamination occurred several times during analyzer setup. The manufacturer varied the column temperature on several occasions to find the best operating condition. This uncertainty in column operation may have been responsible for the zero offset and perhaps some of the elevated responses across the range of concentrations sampled.

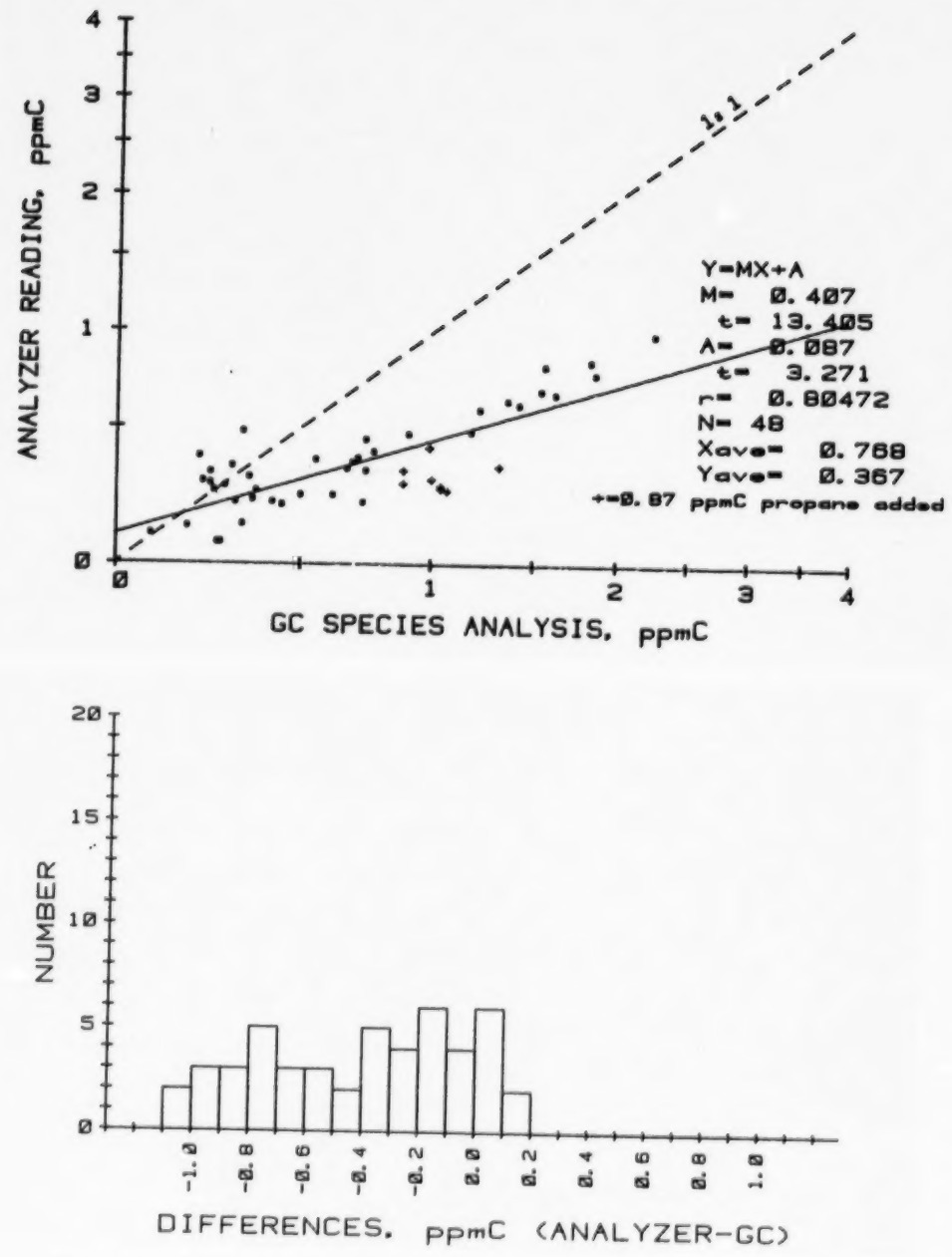

Figure 38. Comparison of ambient air NMOC measurements from the HNU (propane equivalent calibration) and manual GC-FID.

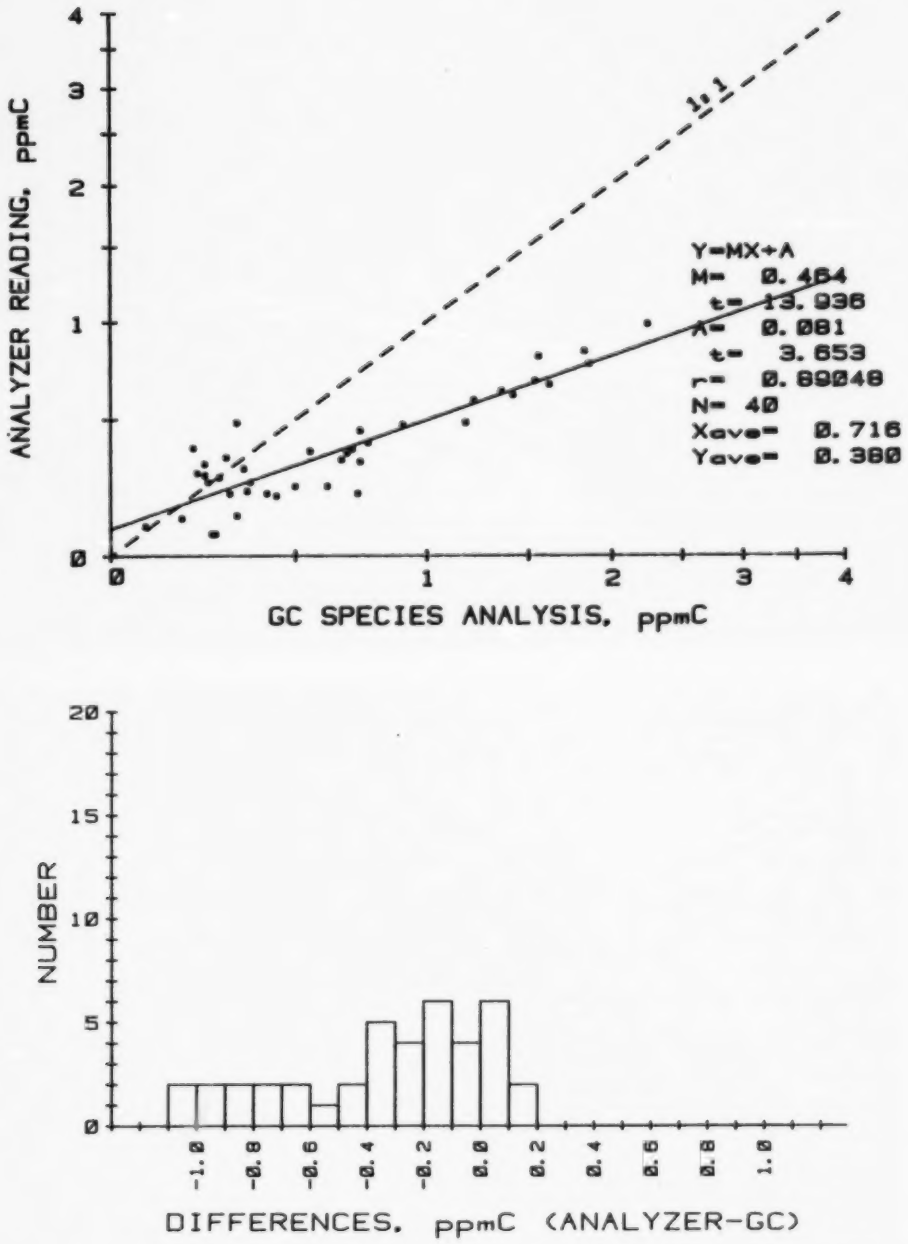

Figure 39. Comparison of ambient air NMOC measurements (excluding propane-spiked samples) from the HNU (propane equivalent calibration) and manual GC-FID.

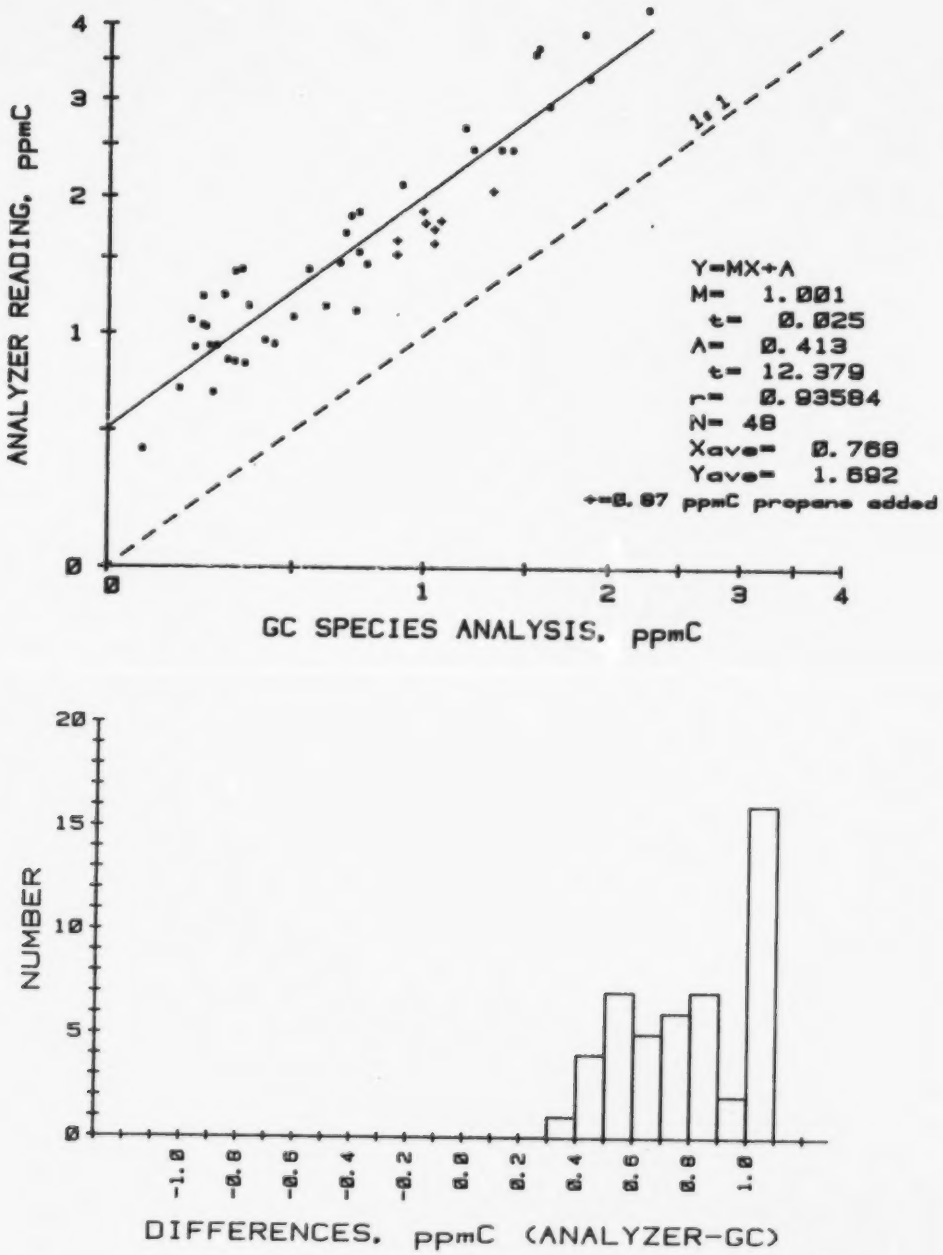

Figure 40. Comparison of ambient air NMOC measurements from the Byron and manual GC.

Intercomparison of Automated Analyzers

The nonconventional automated analyzers were compared using orthogonal regression. Scatter plots of the comparisons are illustrated in Figure 41, along with the estimates of the intercept and slope of the regression line. In the upper diagram, the HNU measurements are adjusted, as usual, to propane (0.85 correction factor); in the lower diagram, the measurements remain referenced to 2-methylpropene (1.0 correction factor). Byron measurements are directly calibrated to propane. Data from the entire study (days 211 through 292) are included in the comparisons, since there was no indication that the analyzers performed better during part of the period, as was the case for the conventional analyzers. Obviously, the response of the HNU is much less than that of the Byron regardless of the standard to which HNU is referenced.

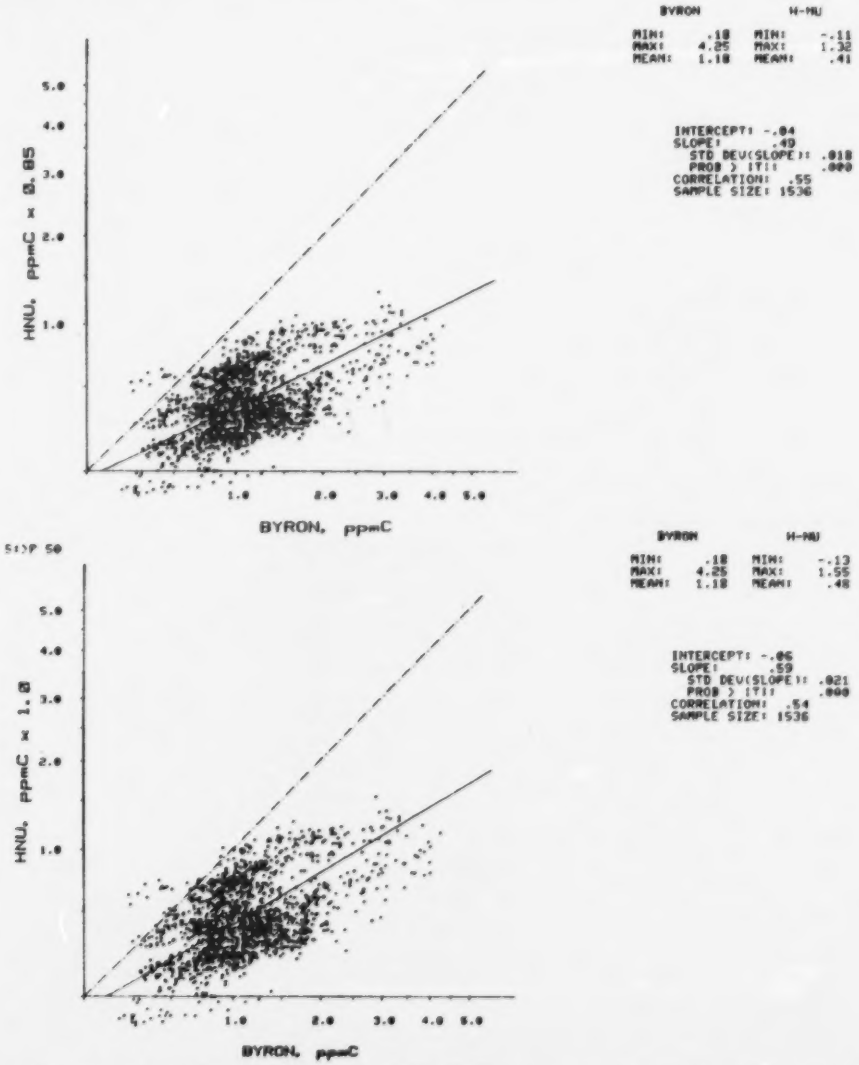

Figure 41. Comparison of ambient air NMOC measurements from the Byron and HNU (all measurements are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 211 through 292).

COMPARISON OF NONCONVENTIONAL VERSUS CONVENTIONAL AUTOMATED ANALYZERS

To compare the nonconventional analyzers to the conventional analyzers and quantify their differences, scatter diagrams of hourly NMOC measurements of the ambient air are plotted by analyzer pairs in Figures 42 through 49. Each figure shows the relationship between a nonconventional and a conventional analyzer. Orthogonal regression analysis is used to quantify the relationships and compute the slope and intercept of the correlation curve. Data from the limited data set are included in the comparisons.

Figures 42, 43, 44, and 45 show the relationship between the HNU and each conventional analyzer. Each figure shows the HNU to have a somewhat elevated intercept, a depressed response, and a correlation significantly lower than the conventional analyzers. The relationships depicted are similar to those with the manual GC-FID. Because of the depressed response, additional comparisons were performed in which the HNU response was not referenced to propane (lower plot in each figure). By eliminating the correction factor of 0.85, the HNU response is referenced to isobutylene. This evaluation showed an increase in the HNU's response; however, the response continues to be significantly depressed.

Figures 46, 47, 48, and 49 illustrate the relationship between the Byron and each conventional analyzer. In each plot, Byron shows an elevated intercept, an elevated response, and a relatively poor correlation. These results are similar to the results from the comparisons with the manual GC-FID.

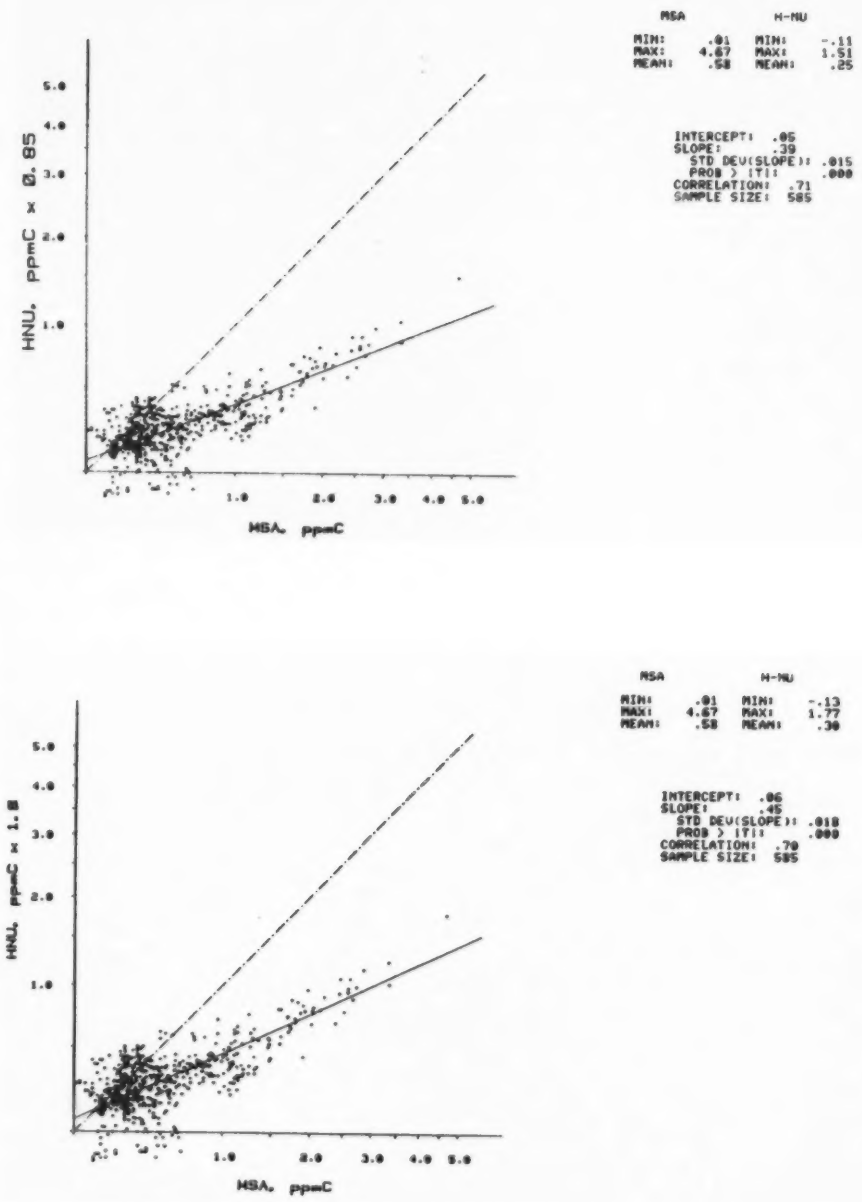

Figure 42. Comparison of ambient air NMOC measurements from the MSA and HNU (all measurements are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

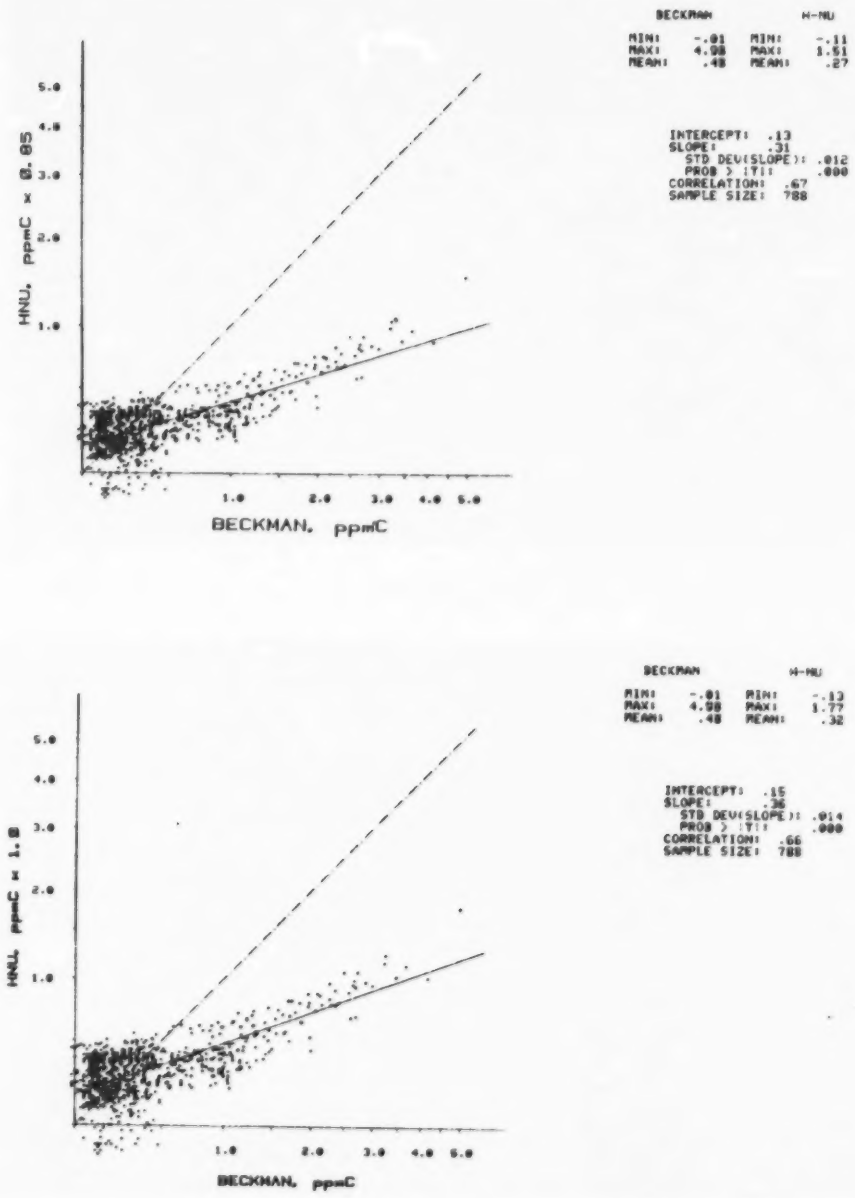

Figure 43. Comparison of ambient air NMOC measurements from the Beckman and HNU (all measurements are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

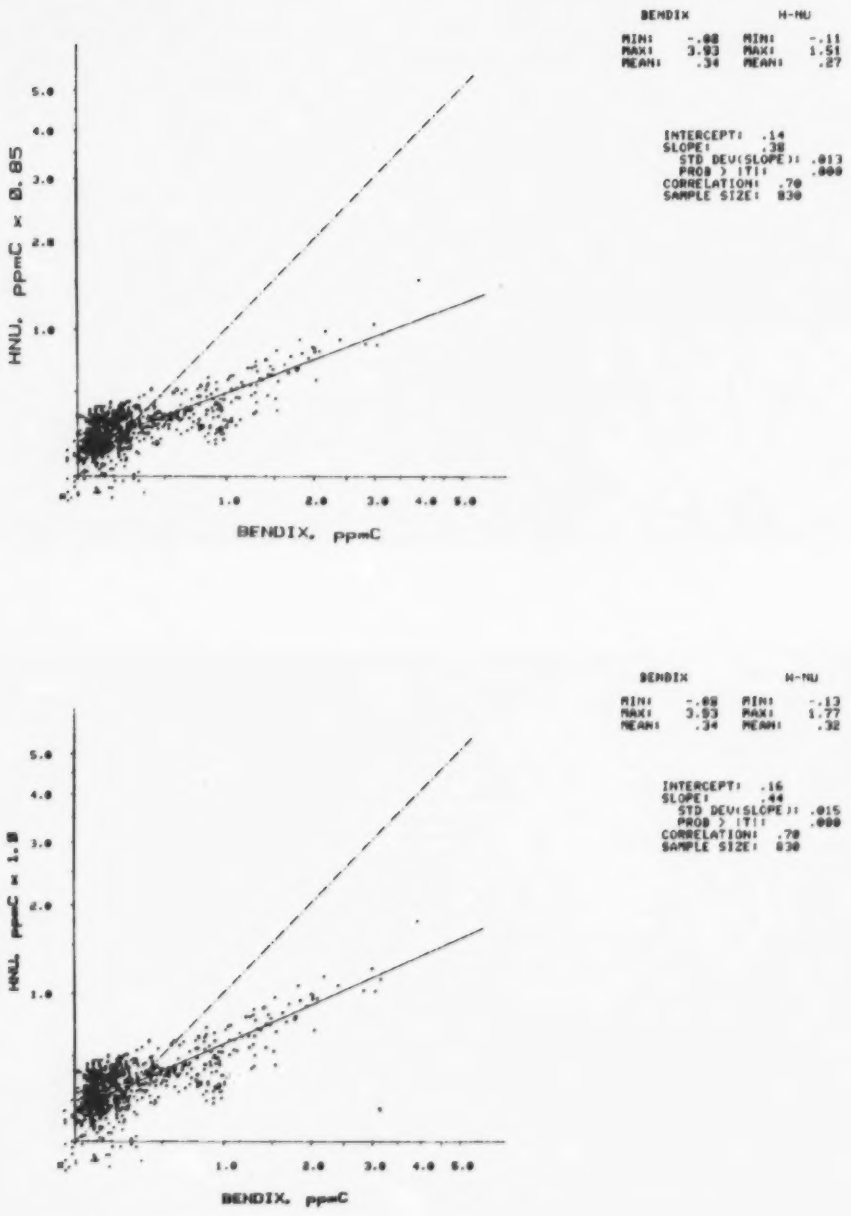

Figure 44. Comparison of ambient air NMOC measurements from the Bendix and HNU (all measurements are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

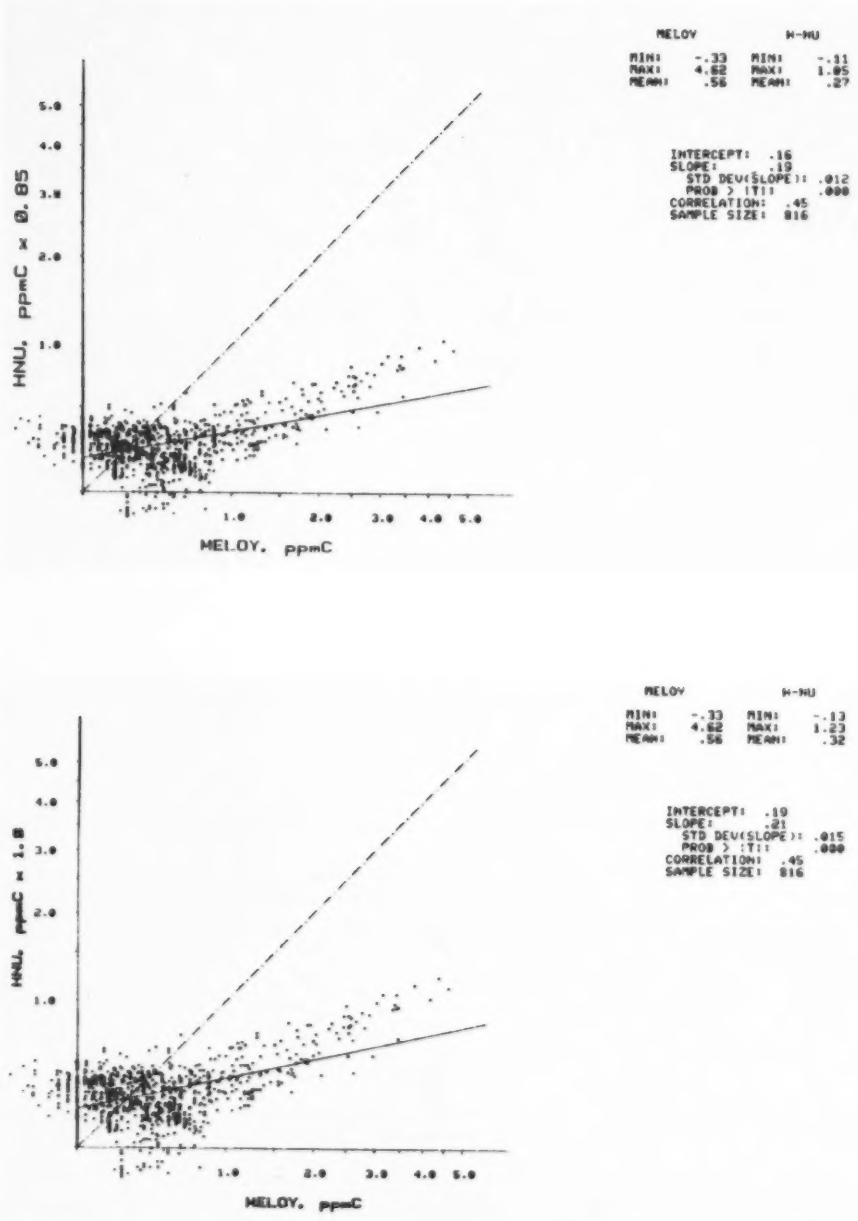

Figure 45. Comparison of ambient air NMOC measurements from the Meloy and HNU (all measurements are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

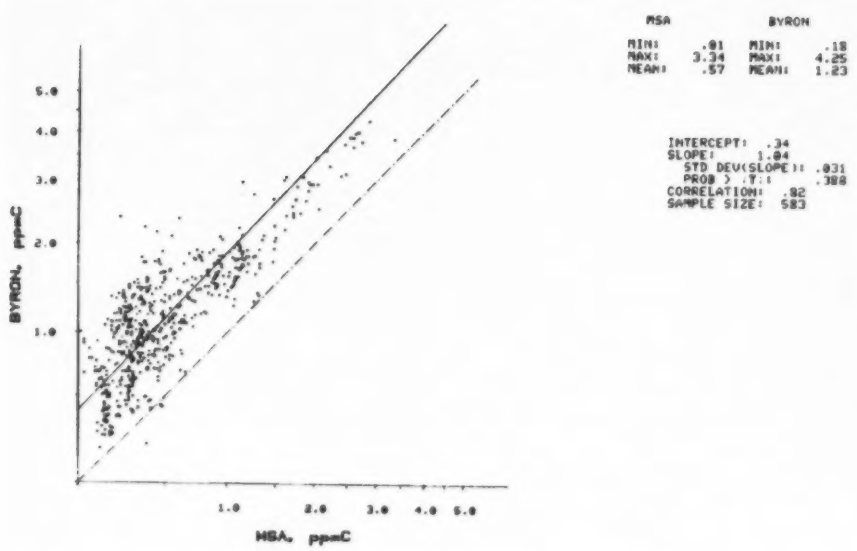

Figure 46. Comparison of ambient air NMOC measurements from the MSA and Byron (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

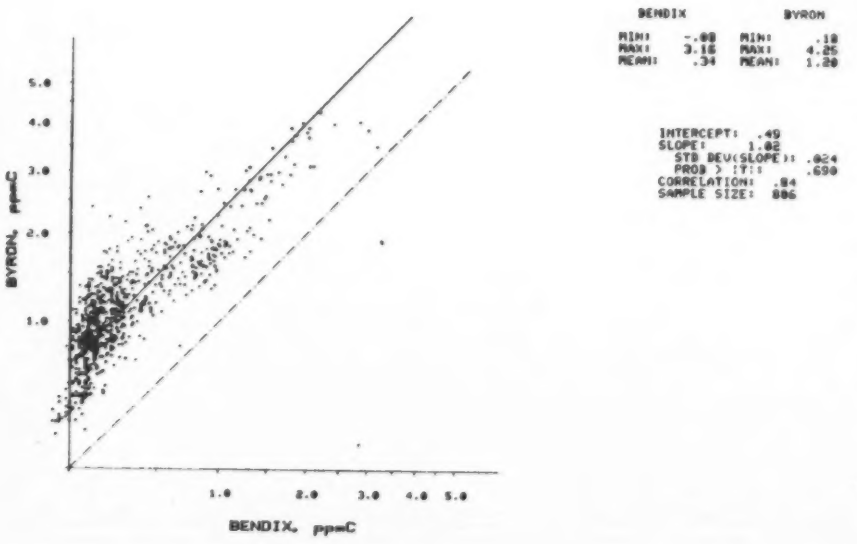

Figure 47. Comparison of ambient air NMOC measurements from the Bendix and Byron (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

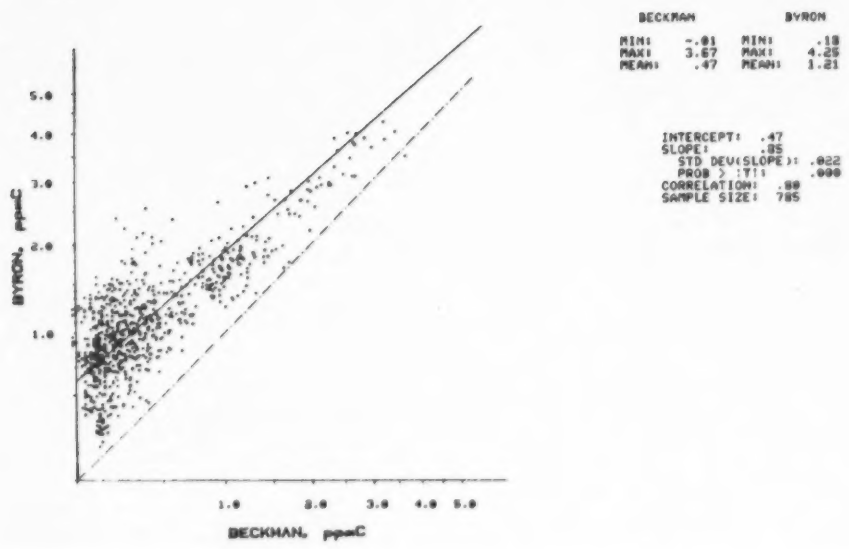

Figure 48. Comparison of ambient air NMOC measurements from the Beckman and Byron (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

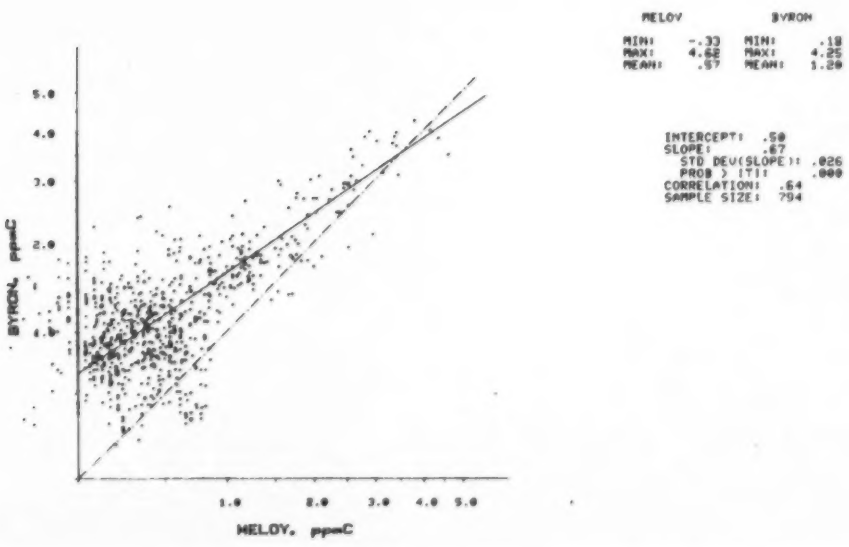

Figure 49. Comparison of ambient air NMOC measurements from the Meloy and Byron (all measurements are referenced to propane and are corrected for zero and span drift; comparisons are by orthogonal regression correlation; days 252 through 292).

COMPARISON OF CATALYTIC VERSUS CHROMATOGRAPHIC SEPARATION OF METHANE

The Bendix and Beckman analyzers separate methane from total hydrocarbons chromatographically; the MSA and Meloy analyzers use catalytic separation. To determine if the measurements produced by the catalytic separation technique were equivalent to the chromatographic separation measurements, an analysis of variance was performed on the logarithmically transformed data. The results of the statistical analysis indicated the measurements from the two separation techniques were equivalent at a 5 percent probability level.

SECTION 5

REFERENCES

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APPENDIX A

FREQUENCY DISTRIBUTION OF DIFFERENCES

During 82 days of ambient monitoring, hourly nonmethane organic concentrations were recorded on each analyzer. Orthogonal regression of each analyzer pair was performed, and the results are summarized in Section 4.

This appendix contains further analysis of these data to illustrate the differences among NMOC analyzers monitoring within specific concentration ranges (0.2 to 0.5 ppmC, 0.5 to 1.0 ppmC, 1.0 to 2.0 ppmC, and greater than 2.0 ppmC). Figures A-1 through A-15 illustrate the differences between all possible analyzer pairs. For example, Figure A-1 contains four separate bar graphs depicting differences between Bendix and MSA responses. The top left bar graph, consisting of a sample size of 390 hourly averages, illustrates analyzer differences within the 0.2 to 0.5 ppmC range based on 81 days of ambient data. The bar graph peak is located approximately 0.15 ppmC below zero and contains 28 percent of the data. Most of the remaining differences lie further to the negative side of this peak. This bar graph indicates that 28 percent of the Bendix responses are 0.15 ppmC lower in the 0.2 to 0.5 ppmC concentration range than the MSA responses. Examination of the remaining three bar graphs shows the differences to be negative, regardless of the pollutant concentration. Also, as the concentration increases, the differences become more random and the sample size becomes smaller. (To verify this interpretation, examine Figure 29 in Section 4. Note that the regression curve of Bendix versus MSA is always below the X=Y axis and that the intercept is approximately -0.15 ppmC.)

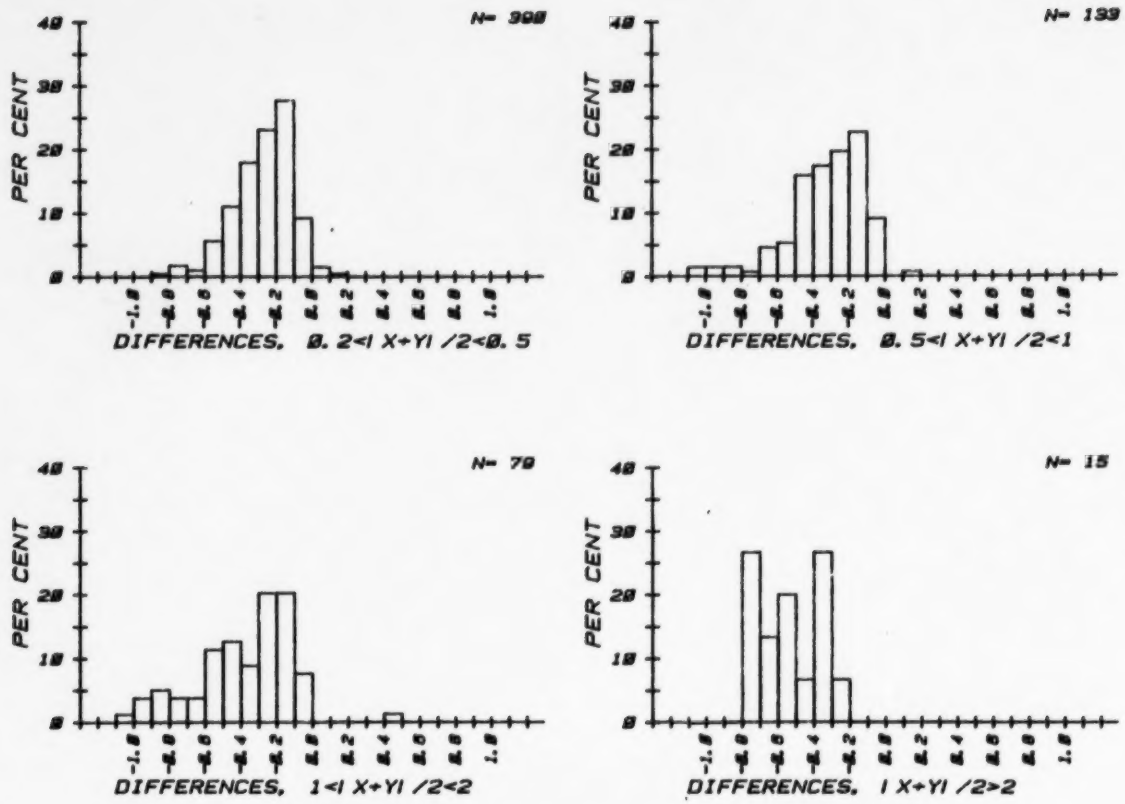

Figure A-1. Frequency distribution of differences between Bendix and MSA by concentration levels.

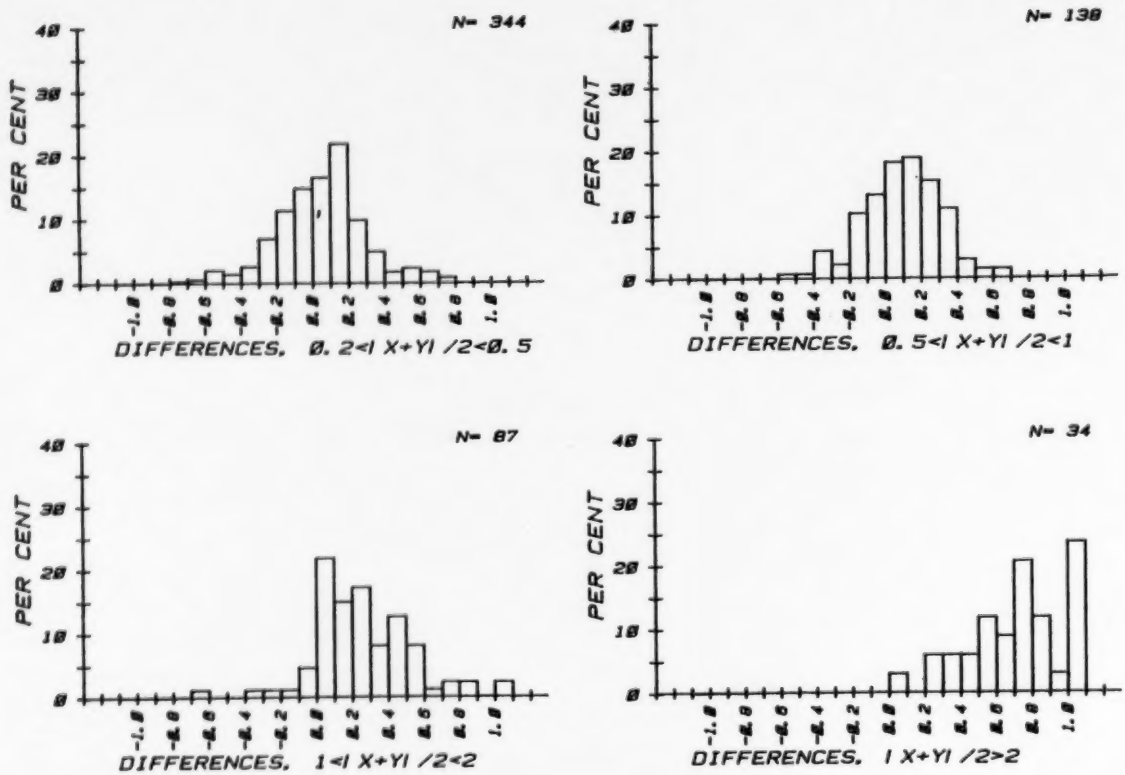

Figure A-2. Frequency distribution of differences between Meloy and MSA by concentration levels.

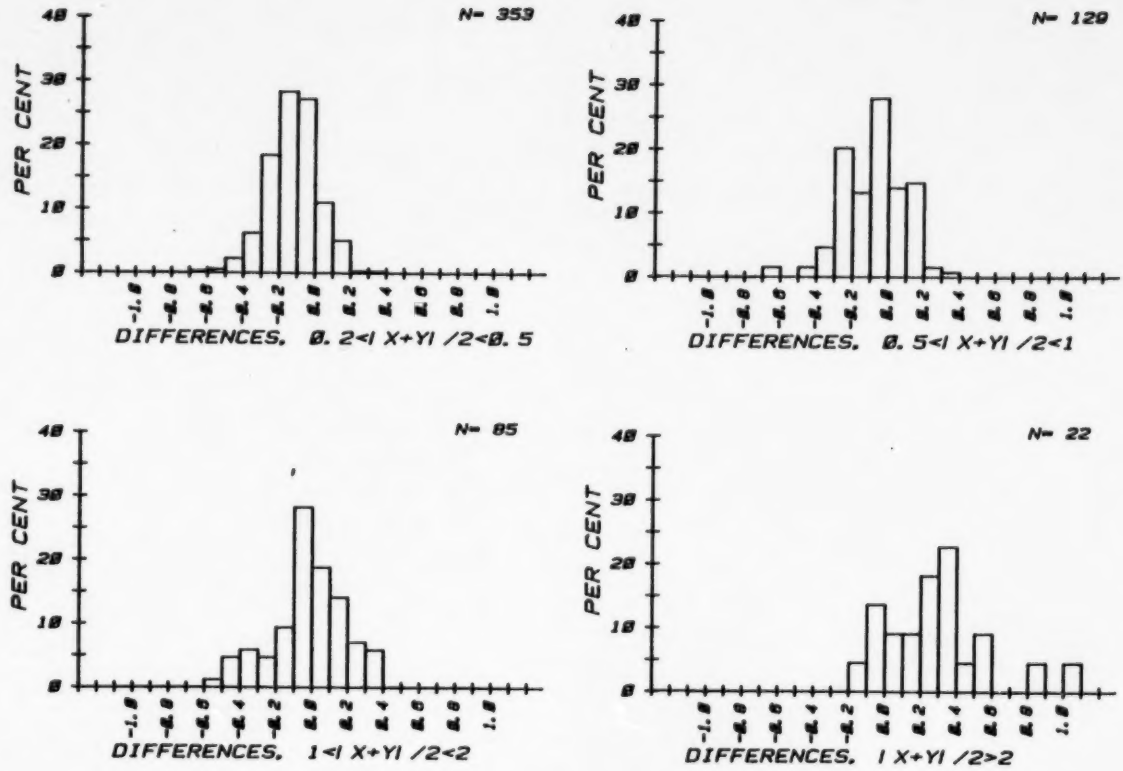

Figure A-3. Frequency distribution of differences between Beckman and MSA by concentration levels.

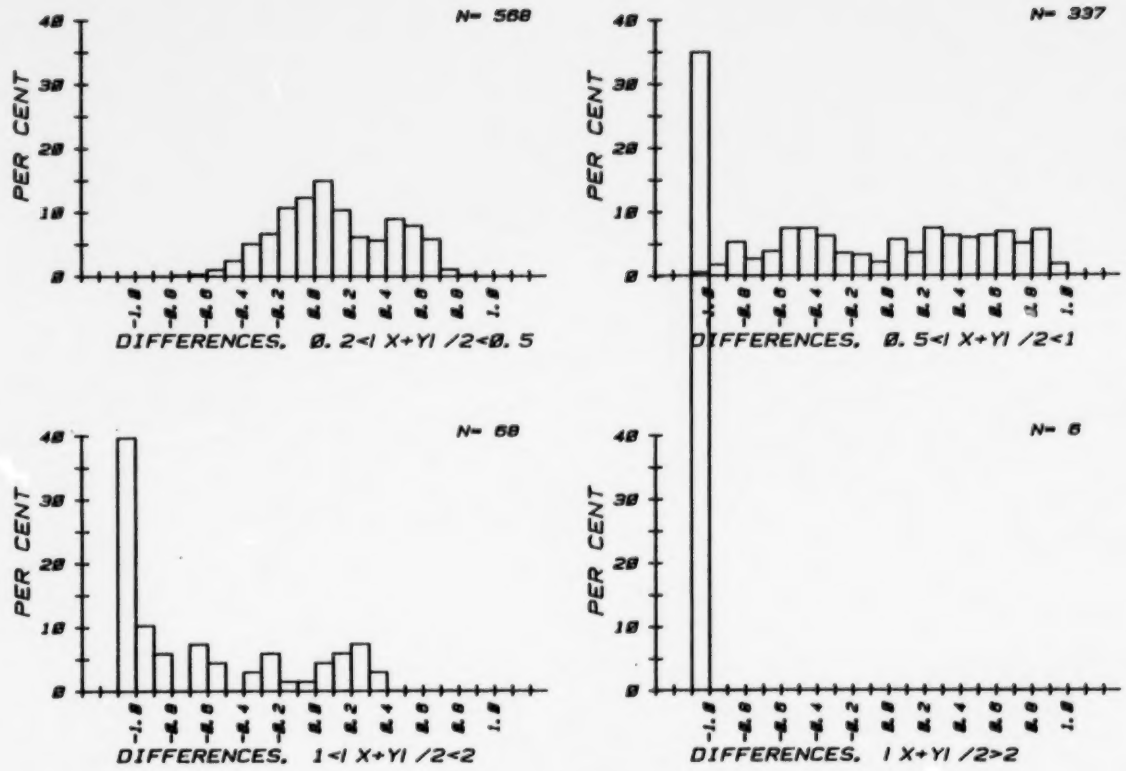

Figure A-4. Frequency distribution of differences between HNU and MSA by concentration levels.

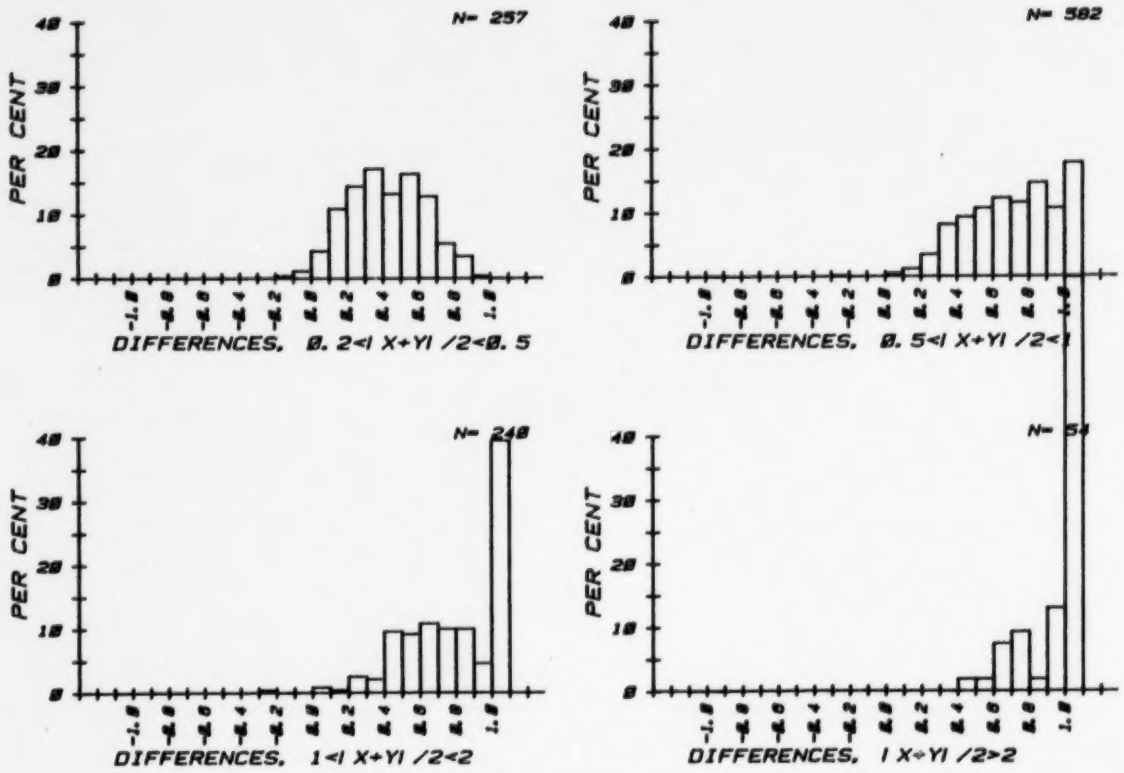

Figure A-5. Frequency distribution of differences between Byron and MSA by concentration levels.

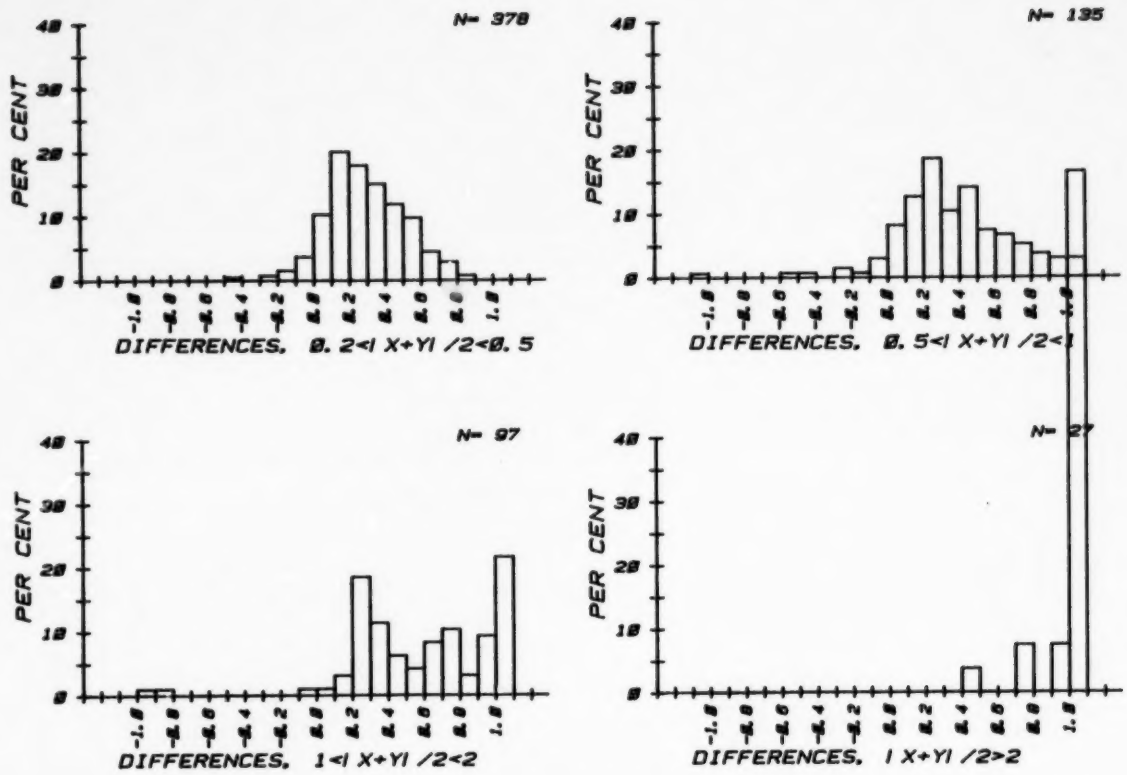

Figure A-6. Frequency distribution of differences between Meloy and Bendix by concentration levels.

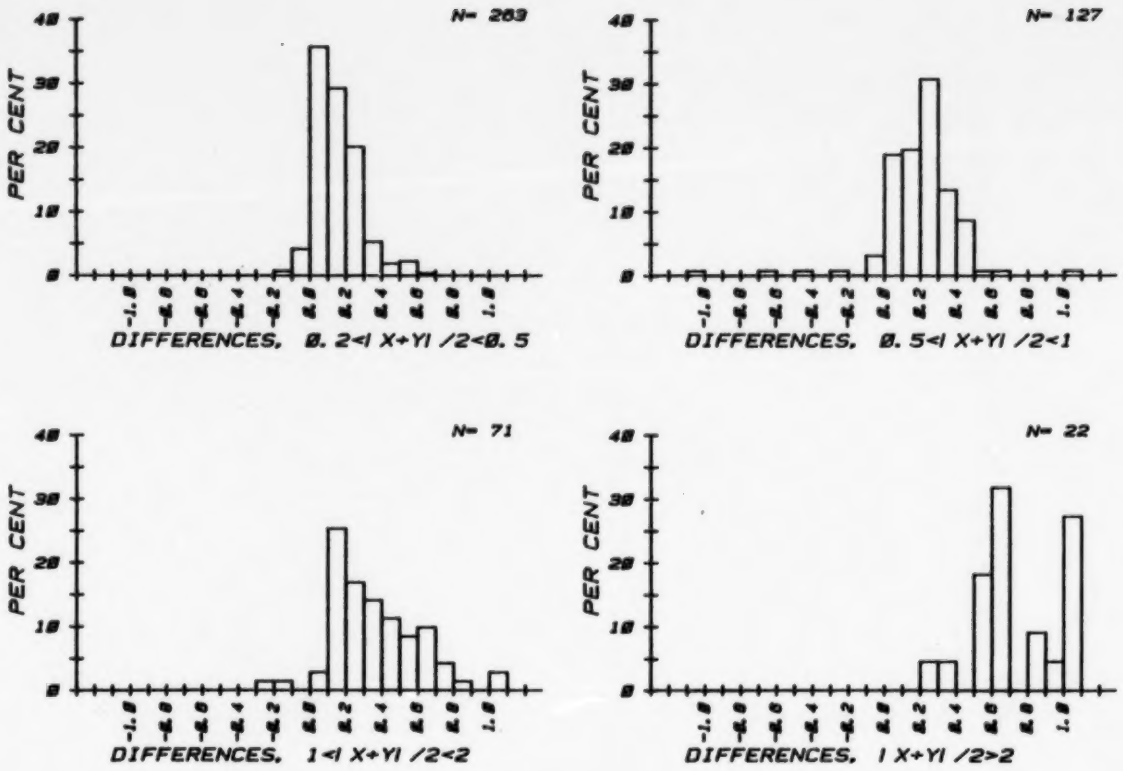

Figure A-7. Frequency distribution of differences between Beckman and Bendix by concentration levels.

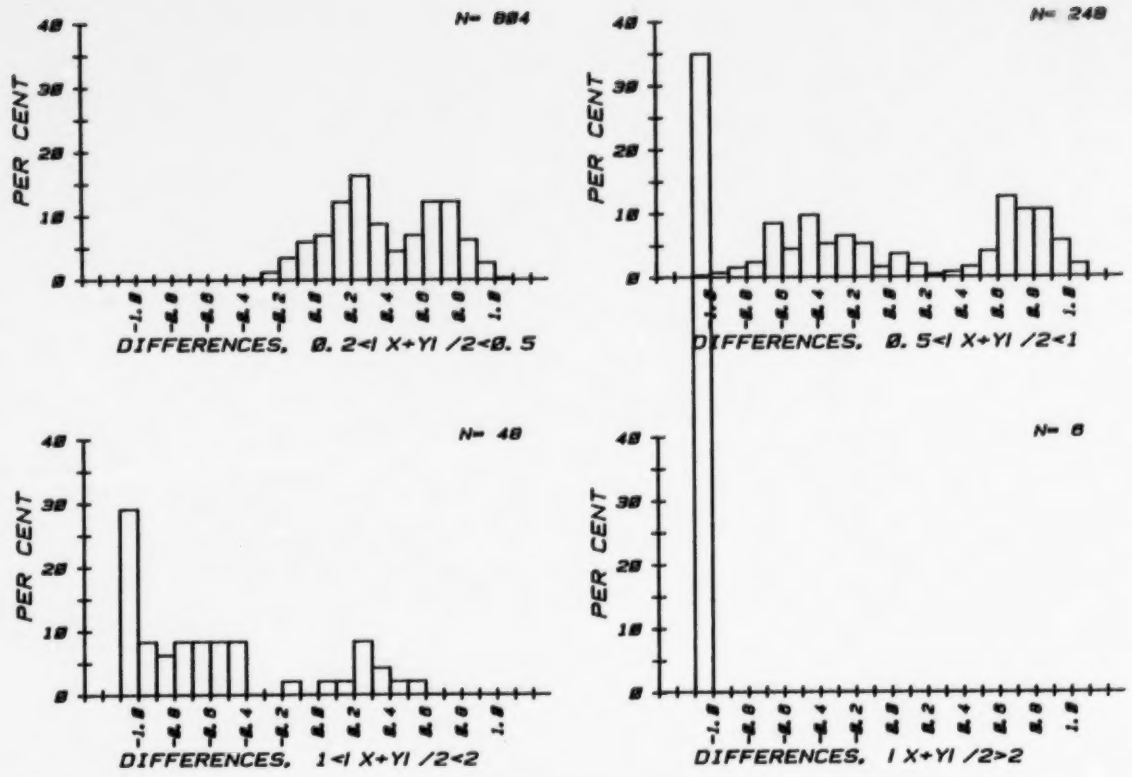

Figure A-8. Frequency distribution of differences between HNU and Bendix by concentration levels.

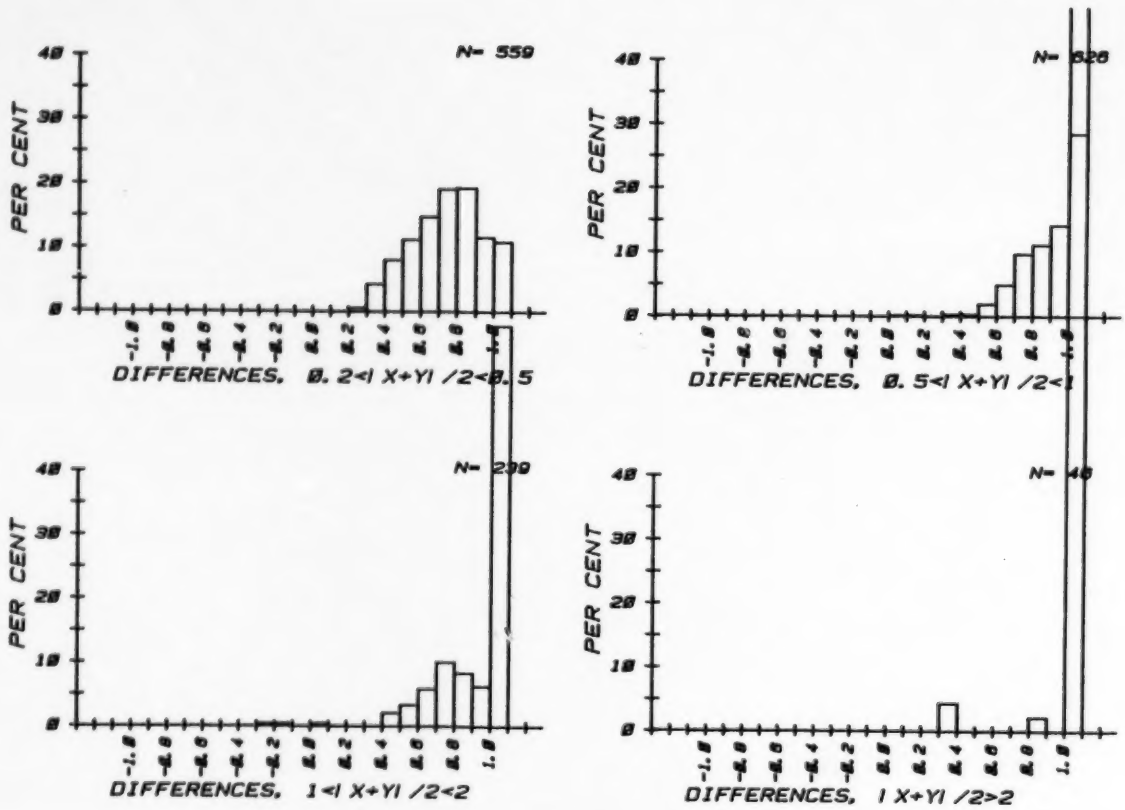

Figure A-9. Frequency distribution of differences between Byron and Bendix by concentration levels.

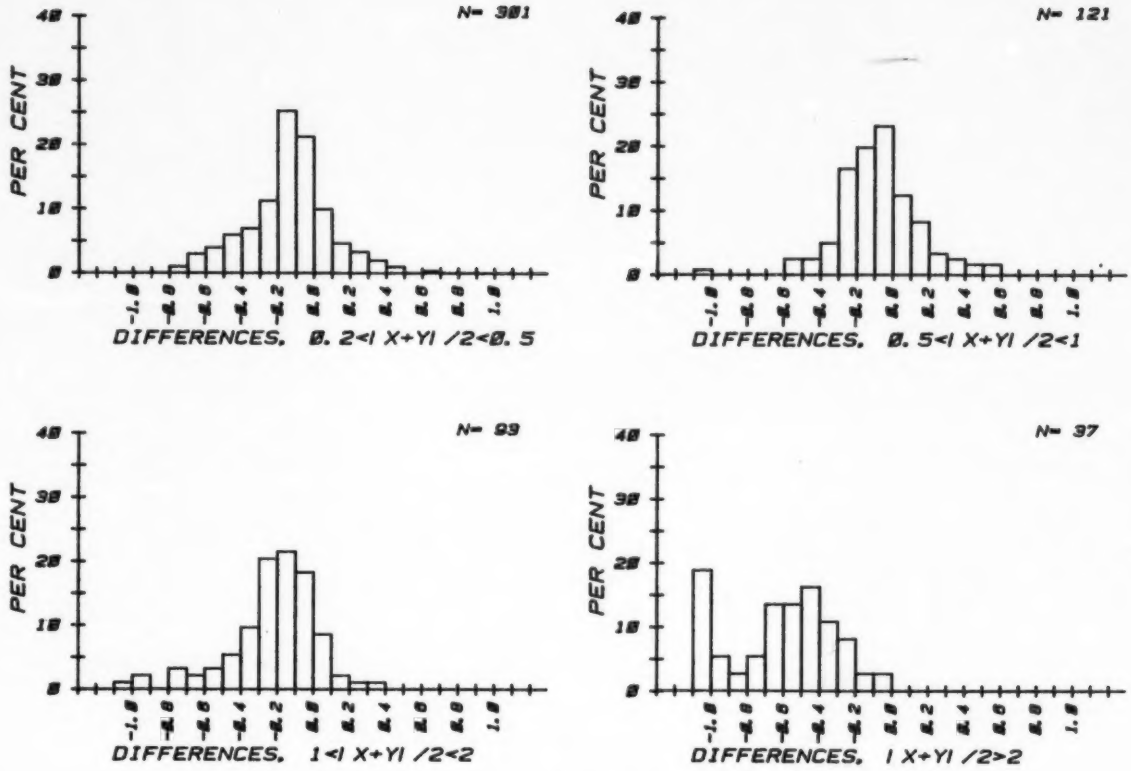

Figure A-10. Frequency distribution of differences between Beckman and Meloy by concentration levels.

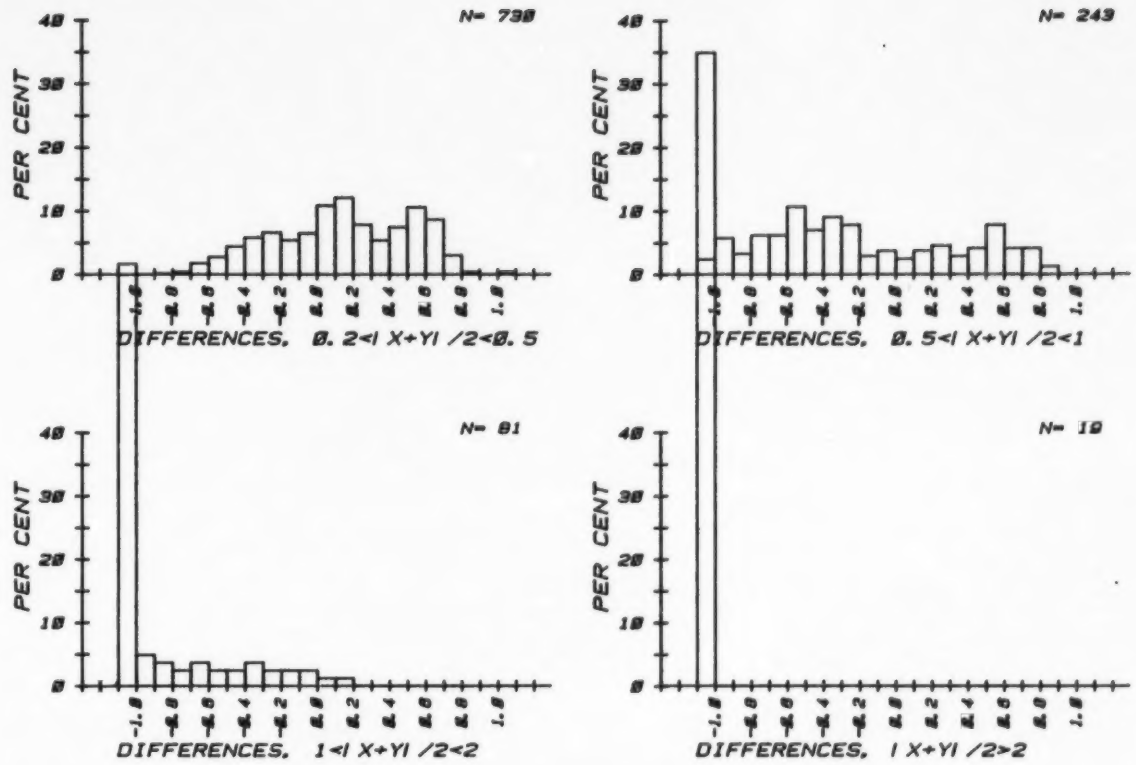

Figure A-11. Frequency distribution of differences between HNU and Meloy by concentration levels.

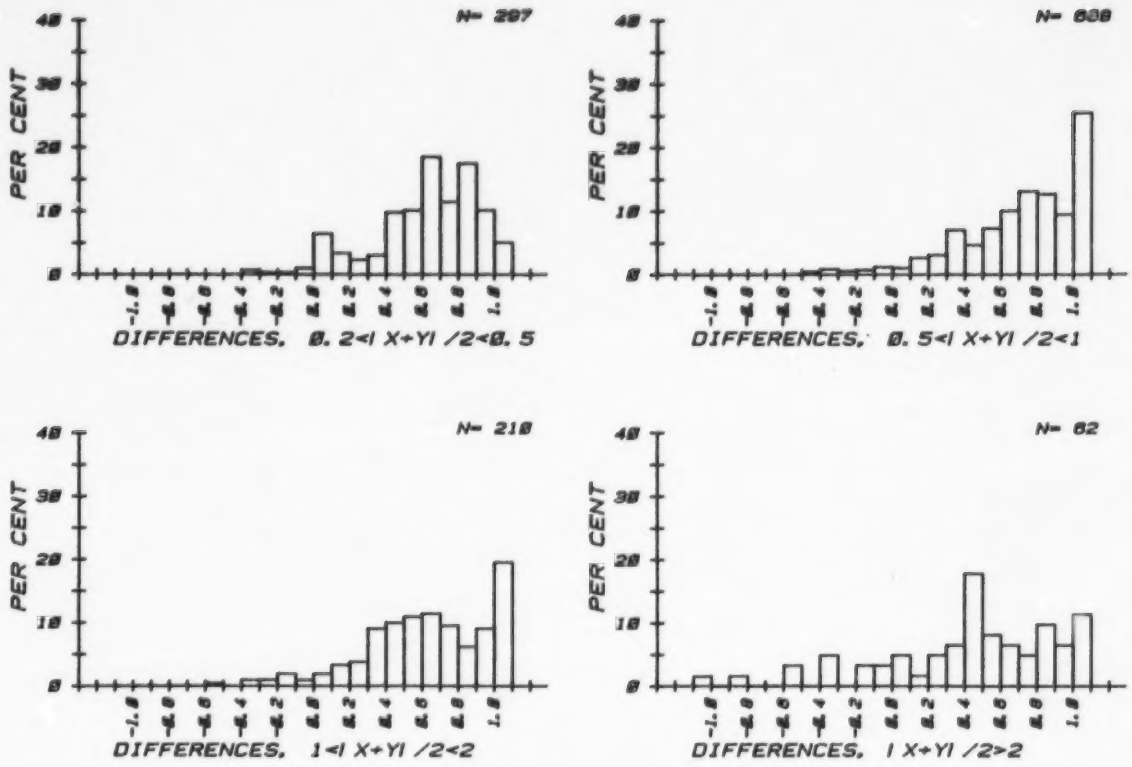

Figure A-12. Frequency distribution of differences between Byron and Meloy by concentration levels.

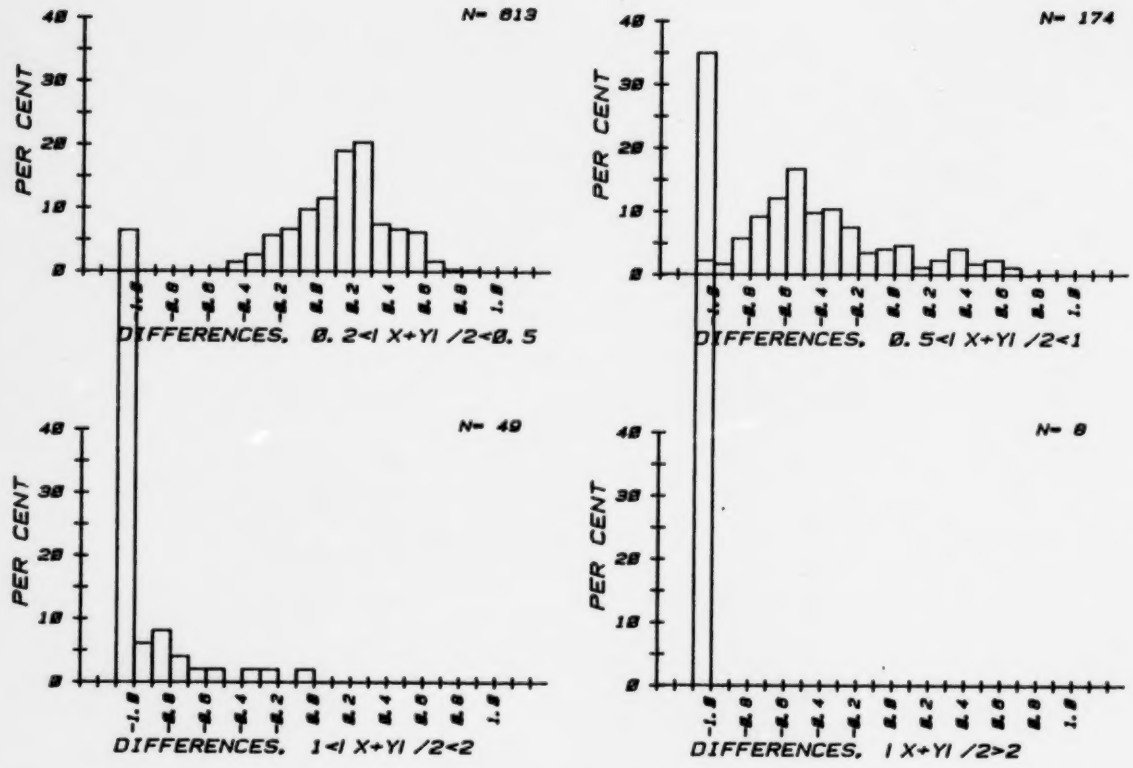

Figure A-13. Frequency distribution of differences between HNU and Beckman by concentration levels.

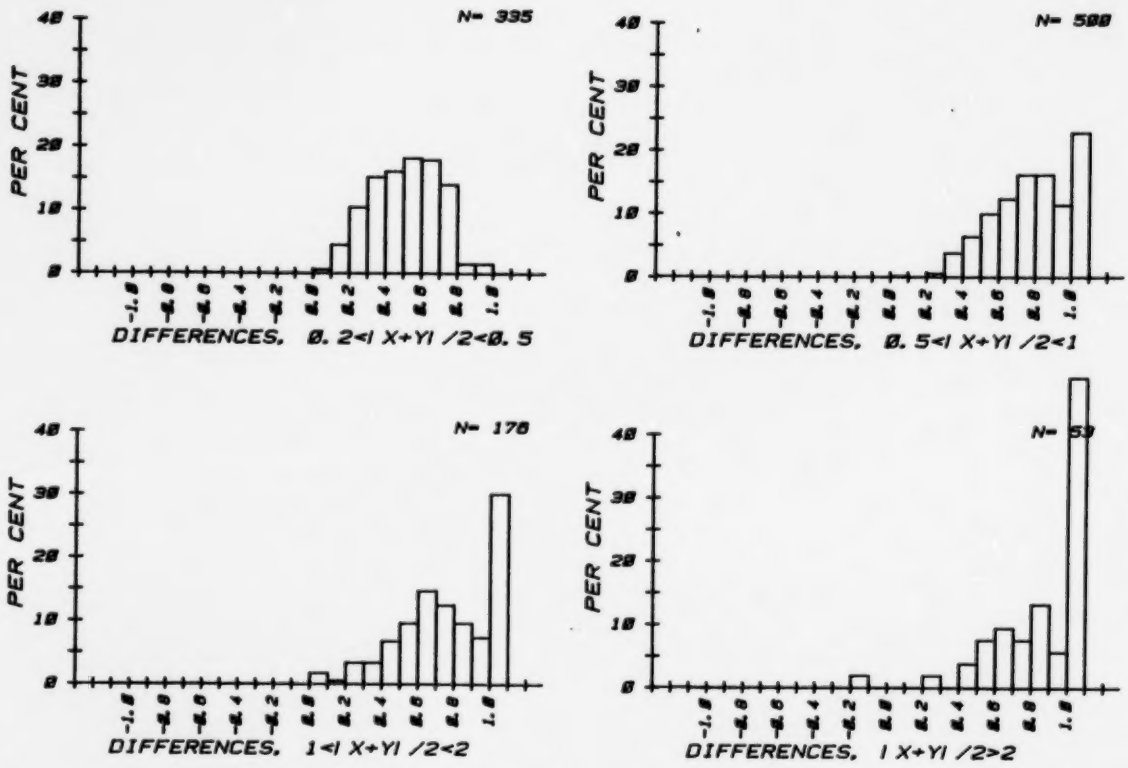

Figure A-14. Frequency distribution of differences between Byron and Beckman by concentration levels.

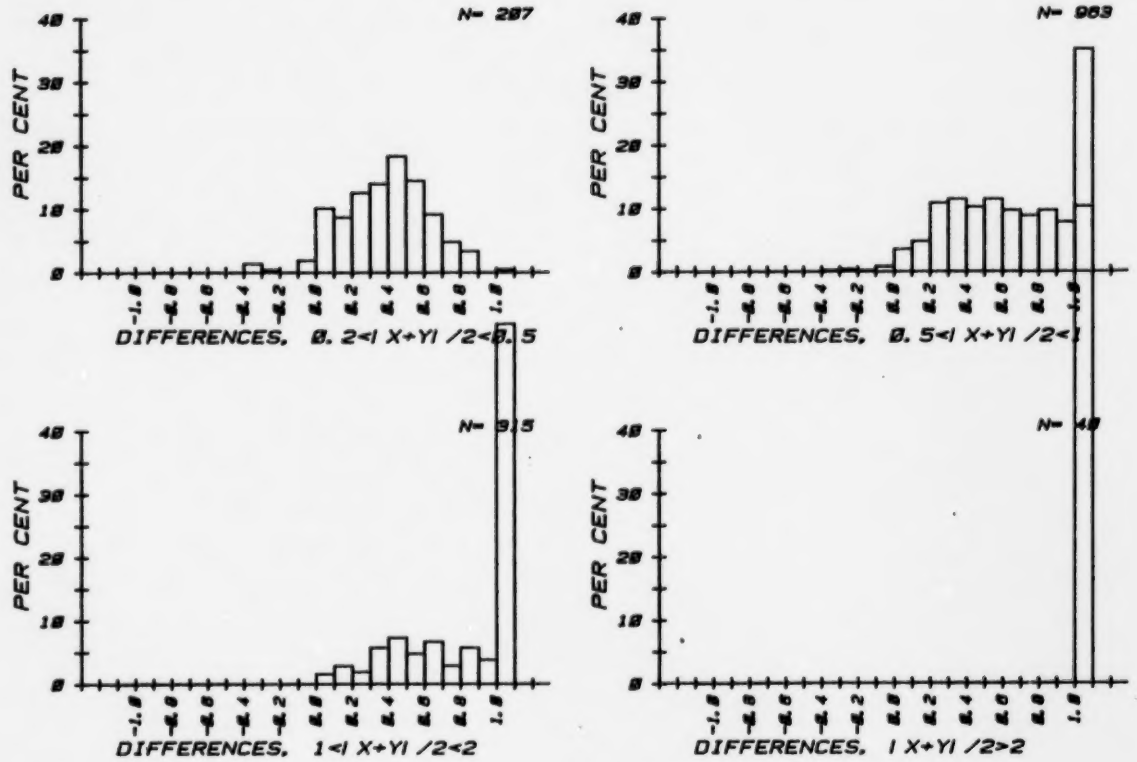

Figure A-15. Frequency distribution of differences between Byron and HNU by concentration levels.